



# CHEMICAL ABSTRACTS

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## 1—APPARATUS

C. G. DERRICK

Apparatus for use in the combustion analysis of volatile hygroscopic liquids. J. B. SHORSMITH. *J. Soc. Chem. Ind.* 42, 57-8T(1923).—The app. has the following features: (1) the liquid is expelled from the containing tube by means of the expansion of a bubble of air; (2) the capillary is broken inside the tube; and (3) the whole app. is contained in the combustion tube proper. A usual capillary tube is connected by a capillary opening to a larger bulb, which acts as the air container. The capillary is then sealed and inserted into a glass tube constricted in the middle and having the ends bent up. The outlet end of the combustion furnace is heated to cherry-redness and the app. introduced. The bent capillary is broken by pressure applied to the constricted glass tube. The stopper of the combustion tube is immediately placed and air slowly passed. The air carries over the vapor of the liquid slowly. As the combustion proceeds the heat drives out the last traces of liquid and the whole is brought to redness. Good results were obtained on  $\text{Et}_3\text{BO}_4$ .

W. H. BOYNTON

Vacuum receiver for fractional distillation apparatus. PAUL KLEBS. *Z. angew. Chem.* 36, 134(1923); 1 cut.—The app. consists of superposed vessels, connected by pipes with cocks, in which the fractions are caught. The distillate enters the top vessel and flows to the lowest which, at the proper time, is cut off from the next higher by closing the cock, etc. Provision is made for emptying the vessels without stopping the distn.

J. H. MOORE

The Arca Regulator. PHILIP SANDFORD. *Gas J.* 161, 453-5(1923).—The Arca Regulator is a sensitive, automatic, app. for use in connection with the control of thermal, chem. or periodic operations, or of pressures. The principle on which it operates depends upon an impulse taken from whatever physical property is to be regulated, applied against a pivoted lever inside a relay in such a way as more or less to suppress a small jet of water, thereby increasing or decreasing the pressure of water under the diaphragm of the pilot valve, so as to manipulate a plunger which admits water into or out of a hydraulic pressure cylinder, and thus to operate valves in such a manner that the required physical condition to be controlled is maintained const. The water pressure required may be from 8 to 80 lb. By means of this app. a temp. control of  $1^\circ \text{F. max.}$  variation on a by-product plant can be guaranteed, or a pressure of  $\pm$  or  $-1/40$  in. water gage in a retort-house hydraulic main, or a pressure of  $\pm$  or  $-1$  mm. in a coke oven. It has been successfully applied for the regulation of the make of gas in a producer-gas plant. Details of construction are given.

J. L. WILEY

Further investigations for determining the efficiency of rapid dialyzers. A. GUTBIER, J. HUBER AND W. SCHIEBER. *Chem.-Ztg.* 47, 100-10(1923).—With good tap water, 80-90% of the electrolytic impurities may be dialyzed from a colloid, with the app. described (cf. C. A. 16, 3236). For the most efficient operation, it is recommended to use 100 r.p.m. for the speed of the dialyzer and 5 l. per hr. for the rate of the solvent liquid.

H. C. PARKER

Apparatus for dispensing concentrated sulfuric acid and sodium hydroxide solutions. ROSCOE ABBOTT. *Ind. Eng. Chem.* 15, 493(1923).

E. J. C.

A laboratory dispensing device for heavy and corrosive liquids. A. P. HARRISON. *Ind. Eng. Chem.* 15, 497(1923). \* E. J. C.

A new viscosimeter. P. LÉCOMPTE DU NOÛY. *J. Gen. Physiol.* 5, 429-40(1923).—This app. utilizes the principle of coaxial cylinders. An outer cylinder cntg. the liquid rotates around a plunger immersed in the liquid. There is a direct proportionality between the torque due to the friction exerted by the liquid on the plunger when the outer cylinder is rotating and the rate of rotation. The readings are, therefore, proportional to the rate. The app. is particularly adapted to the measurement of colloidal and physiol. solns. Less than 1 cc. of liquid is required for a measurement. Other advantages are: Rapidity of operation (30 sec. to 1 min. for a reading), accurate temp. control, large range and ease of changing the range, great sensitivity. It can be used as a recording viscosimeter. CHAS. H. RICHARDSON

Apparatus for admitting gas into a vacuum. J. B. JOHNSON AND H. W. WEINHART. *J. Optical Soc. Am.* 7, 175-7(1923).—The app. is in principle an inverted Topley pump carrying a small vol. of gas, trapped between Hg columns in a capillary tube, from a gas container to a low-pressure app. Both sides of app. are provided with adjustable Hg reservoirs so that measured vols. of gas are forced through the capillary tube by inflowing Hg. The range of pressure change with one stroke of Hg piston, assuming 1 mm. bore of capillary, is between 0.003 mm. and 0.25 mm. To prevent contamination of the gas both sides of the app. are first connected by a capillary tube at the top, vacuum is applied and then the connecting tube is sealed off. The gas container already connected to the app. is opened by breaking the internal seal with a steel ball and the app. is ready for use. Means is provided for keeping the pump heated with a Bunsen flame. HOWARD E. BATSFORD

Automatic mercury pump model 1922. G. P. PAMFIL. *Bul. soc. chim. Romania* 4, 57-60(1923).—The pump was developed for removing gases from a vessel and delivering them for measurement and analysis. It consists essentially of a system of glass and rubber tubing in which Hg is transferred from an adjustable glass reservoir to a modified Hempel or Topley pump, passes down through a capillary tube into a receiving vessel, and returns to the original reservoir through a pulsometer. The app. is actuated by a simple water jet and can work indefinitely; it quickly reaches a very high vacuum; all app. of very large capacity can be evacuated, the gas collected and delivered for analysis. HOWARD E. BATSFORD

An improved method for control of temperature and other physical quantities. PAUL E. KLOPSTEG AND W. H. STANNARD. *J. Optical Soc. Am.* 7, 179-86(1923).—The app. described is a mechanism for holding const. within  $\pm 0.14^\circ$  the variation of temp. in a bath of oil. It depends on a regulator with solid elec. contacts, motion of one of which is produced by temp. changes in a strip or helix of "thermostatic" metal (laminae of brass and invar welded together). The line voltage is applied to the heating unit through the regulator and rotating interrupter, an extra heating coil being arranged for permanent connection across the line. The regulator is composed of a helix of invarbrass laminated metal acting, on change of temp., to swing an arm against a fixed contact on an electromagnet, completing the circuit. The interrupter consists of rotating metal cylinder with an insulating segment which periodically opens the circuit. A condenser is added to the circuit to reduce the amt. of arcing at the interrupter. Several advantages are claimed. The same principle is applicable to other phys. quantities such as pressure. HOWARD E. BATSFORD

A new steam superheater for laboratories. KURN VON HAKEN. *Z. angew. Chem.* 36, 134-5(1923).—A description, with 1 cut, of the "Dargatz" app. which will heat steam to  $450^\circ$  with a small gas flame. J. H. MOORE

A few novelties in the chemical stoneware industry. M. KALTENBACH. *Chimie*

*et industrie* 9, 227-32(1923).—Brief description of recent types of fans, pumps, and controlling cocks (for adjusting the flow of corrosive liquids). A. P.-C.

New instrument for testing glue and gelatin jellies (Richardson) 29. A new method of microsublimation (KEMPF) 7. The colloid mill (ANON) 30.

Acetylene generator. W. H. SAUTER. U. S. 1,449,957, Mar. 27.

Mercury vacuum pump. KAZUO KAMITAVASHI and the AOYAGI KENKYUJO. Japan. 40,391, Oct. 21, 1921. Hg is circulated through a rectangular tube fixed vertically. At the middle and lower parts, inlet and outlet orifices are provided. The lower part is exhausted by a suitable vacuum pump and the Hg circulated passes the inlet orifice in the state of mist at high velocity.

Hydrometer. C. M. LARSON. U. S. 1,449,334, Mar. 20. A hydrometer or "dilutometer" is provided with an adjustable scale clamped to its stem which can be adjusted to different relative gravities for indicating the strength of crank-case lubricating oil or other solns. or liquids.

Electric pyrometer. H. E. IVES. U. S. 1,449,512, Mar. 27. A photocell. cell receives rays through a diaphragm and a vacuum tube is used for amplification of the elec. current before it acts on a recording device.

Evaporation apparatus. JIROMA YAMASHITA. Japan. 40,395, Oct. 21, 1921. Structural features.

Apparatus for evaporating or distilling solutions. H. BOLLMANN. U. S. 1,449,313, Mar. 20. The app. comprises a boiler and a head, with partitions subdividing the lower portion of the boiler into compartments in vapor-free communication at the tops and having relatively small pipes for carrying liquid from the lower part of one compartment to the upper part of the next succeeding compartment. The liquid is heated to successively higher temps. in the different compartments.

Apparatus for extracting liquids from cotton seed or other materials by pressure and centrifugal action. A. S. KIRSHNER. U. S. 1,449,290, Mar. 20.

Apparatus for filtering compressed air. C. B. PARKER. U. S. 1,450,561, Apr. 3.

Apparatus for purifying gases. A. R. KOLB. U. S. 1,448,126, Mar. 13. The app. is adapted for purifying  $\text{SO}_2$  to remove free S. It comprises a conduit through which the gases flow, a hood arranged in the conduit and a burner for projecting a flame from the hood into the conduit.

Air control for drying apparatus. E. P. HECKEL. U. S. 1,449,115, Mar. 20. In app. for drying *milk* or other materials, a current of air is supplied to the drying chamber at a substantially constant temp. and is so regulated that a fixed drop in temp. is maintained between the air entering and that leaving the drier, in order to produce uniform drying.

Air-testing device. R. H. DAVIS. U. S. 1,447,968, Mar. 13. The device is adapted for testing the freshness of air in rooms or other confined spaces. It comprises a dry-bulb thermometer, a heat-conducting jacket enclosing the bulb end of the thermometer and an incandescent elec. lamp or other device for supplying a constant amt. of heat to the jacket, to cause convection air currents.

Apparatus for gasifying liquid oxygen. W. GENSECKE. U. S. 1,448,590, Mar. 13. A heat-insulated container for liquid O is provided with a valved discharge orifice controlled by a drum.

Oil filter. G. E. PUTNAM. U. S. 1,450,750, Apr. 3.

Decanting device for separating stratified liquids. O. E. HANS. U. S. 1,450,545, Apr. 3. The device is adapted for drawing off a layer of oil superposed upon *salt*  $\text{H}_2\text{O}$ . It comprises a draw-off funnel carried by floats at the surface of the liquid and an

automatic cut-off for stopping the flow when the funnel reaches a liquid layer of a particular density.

Apparatus for spray desiccation of milk or other liquids. S. M. DICK. U. S. 1,450,840, Apr. 3.

## 2—GENERAL AND PHYSICAL CHEMISTRY

GEORGE L. CLARK

The placing of the radicals in the periodic system. A. RYD V MIRO. *Helvetica Chim. Acta* 6, 188-91(1923).—Those radicals whose chem. properties are similar to those of the elements may be assigned to their proper groups in the periodic table by means of the following rule. The order no. of a radical is given by the sum of the at. nos. of the elements of which it is composed, diminished by twice the no. of valences which were shared in its formation. The order no. thus calcd. will be the at. no. of an element in a certain group. The chem. properties of the radical will be similar to those of the elements of this group. E. g., the order no. of  $\text{NH}_4$  is  $(7 + 4) - (2 \times 4) = 3$ , which is the at. no. of Li, and  $\text{NH}_4$  has properties characteristic of the alkali metals. For CN, the order no. is  $(6 + 7) - (2 \times 2) = 9$ , the at. no. of F, and the chem. properties of CN are similar to those of the halogens. For NO,  $(7 + 8) - (2 \times 2) = 11$ , the at. no. of Na, and the similarity of NO to the alkali metals is evident in compds. such as  $\text{NOCl}$  and  $\text{NOHSO}_4$ . If  $\text{F}_2$  is considered to be a radical, its order no. is  $(2 \times 9) - (2 \times 1) = 16$ , the at. no. of S. This corresponds to the formation of acid salts by  $\text{H}_2\text{F}_2$ , the small ionization const. of  $\text{H}_2\text{F}_2$ , and the replacement of O by F in acids without greatly changing their properties. For CO,  $(6 + 8) - (2 \times 2) = 10$ , the at. no. of Ne. This corresponds the stable behavior of CO, despite the free valences which it probably has. Other examples are given.

R. H. LOMBARD

The crystal structure of tin tetraiodide. R. G. DICKINSON. *J. Am. Chem. Soc.* 45, 958-62(1923).—The crystal structure of  $\text{SnI}_4$ , investigated by means of Laue and spectral photographs, is such that there are 8 mols. in a cubic unit having  $d_{100} = 12.23$  Å. The I atoms cannot all be in equiv. positions. The space group symmetry is  $T_d^2$ . Probably the Sn atoms are at points equiv. to  $(uuu)$  and the I atoms at points equiv. to  $(vrv)$  and  $(xyz)$ . The values  $u = 0.129$ ,  $v = 0.253$ ,  $x = 0.009$ ,  $y = 0.001$ , and  $z = 0.253$  account for the intensity data and surround each Sn atom tetrahedrally by I atoms. The structure may, therefore, be considered mol. in the same sense that org. mols. retain their identity in space lattices. Certain anomalous Laue spots possibly related to effects observed by Clark and Duane (*C. A.* 16, 4134) and McKeehan (*C. A.* 17, 681) are not interpreted.

G. L. CLARK

Modification of the powder method of determining the structure of metal crystals. E. A. OWEN and G. D. PRESTON. *Proc. Phys. Soc. London* 35, 101-8(1923).—The Bragg method of analyzing powders by means of the ionization spectrometer (*C. A.* 15, 3421) is extended to plates of metals. Al, Mg, Fe, Cu and Pb plates were examined in detail. The results agree with those of Hull. The plates were subjected to previous heat treatment in order to produce a mass of small crystals, 1 mm. or less across.

G. L. CLARK

The crystalline structure and properties of tartaric acid. W. T. ASTBURY. *Proc. Roy. Soc. (London)* 102A, 506-28(1923).—By means of exceedingly ingenious interpretation of X-ray spectrometer data the crystal structure of active tartaric acid is obtained. The unit monoclinic cell contains 2 mols.;  $a$ ,  $b$  and  $c$  are, resp., 7.693, 6.037 and 6.195 Å.; the 010 and 001 spacings show only  $1/2$  the calcd. spacings. A mol. serving in this case as the structural unit is placed at each of the corners of the unit cell and other mols. at points on a dyad axis at the center of 100 faces so that 010 and 001 spac-

ings are halved but the 100 spacing is not. In order to account for the single element of crystallographic symmetry, a unique dyad axis parallel to the crystallographic  $b$  axis, the latter mols. must be like those at the corners but rotated through  $180^\circ$  with respect to them. In each mol. of tartaric acid the C nucleus may be represented as a tetrahedral arrangement upon an oblique parallelepiped. Mols. are held together, end to end along an edge of the unit crystal cell, by forces between the H atoms of adjacent (diagonally linked across between successive C nucleus parallelopipeds) hydroxyl groups, one hydroxyl group being carboxylic and the other alc. The plane about which these mol. junctions lie is the plane (100), the only perfect cleavage plane of the crystal. Numerous other properties are compared with the crystal structure. LeBel and van't Hoff's theory of stereoisomerism is in its essentials confirmed and the direct link between crystallographic enantiomorphs and the chem. stereoisomers is revealed. Since the diffraction of X-rays is a summation effect of all planes concerned, there can be no difference between the diffraction patterns produced by 2 enantiomorphous (mirror image) forms. Optical activity must be a property of the mol. itself since it is observed in soln. as well as crystals, as contrasted with the rotation by quartz due to spiral arrangement in the crystal itself. The 4 C atoms in the tartaric acid mol. are in an irregular spiral formation, as are also the hydroxyl groups though in an opposite sense. The balance of evidence leads to the conclusion that the dextrorotatory property of ordinary tartaric acid is associated with the C nucleus which alone under all conditions of soln., diln., hydration, etc., possesses a real stability. Such effects as ionization and hydration would tend to destroy the levorotatory action of the hydroxyl spiral; hence it requires the application of the forces which bind mols. into cryst. structure to complete the levorotatory system. These two kinds of spirals, simultaneously present and oppositely twisted in enantiomorphs, afford a simple explanation of the anomalous rotatory dispersion of tartaric acid and many of its derivs.

G. I. CLARK

The relation between molecular and crystal symmetry as shown by X-ray crystal analysis. G. SHEARER. *Proc. Phys. Soc. London* 35, 81-100(1923).—The methods of X-ray analysis enable the no. of mols. associated with the unit crystal cell to be detd. With the help of this information an attempt is made to connect the symmetry properties of the crystal with this no. and with the symmetry properties of the mols. from which the crystal is formed. The symmetry no. for each of the 32 crystal classes is given and is shown to mean the min. no. of asym. mols. necessary in the unit cell to satisfy the symmetry conditions (from 1 in triclinic asym. to 48 in the hexakis octahedral class of the cubic system). The relative orientations and positions of these mols. in the cell are discussed. It is suggested that this symmetry no. is the actual no. of mols. in the cell when the mol. is asym., and that if the mol. possesses symmetry, this symmetry also appears in the crystal, and the no. of mols. in the unit cell are obtained by dividing the symmetry no. of the crystal by the symmetry no. of the mol. Numerous examples in support of these hypotheses are cited.

G. I. CLARK

The behavior of different silicic acids. E. BEHR AND W. URBAN. *Z. angew. Chem.* 36, 57-60(1923).— $\text{SiO}_2$  was pptd. from Na silicate by Patrick's method (C. A. 14, 1776) and washed free of chloride. This was divided into 4 portions which were, resp., dried in vacuum over  $\text{P}_2\text{O}_5$  at  $25^\circ$  until 4.9%  $\text{H}_2\text{O}$  was left (A), heated to const. wt. at  $300^\circ$  (B), ignited at  $1000^\circ$  (C), or evapd. several times with HCl and then ignited as in analysis (D). The hydration and dehydration curves of these materials and of powd. quartz boiled with HCl (E) were detd. The curves for A, B, and C showed hysteresis. The  $\text{H}_2\text{O}$  absorption decreased from A to E. That of activated charcoal was less than that of A or B under any conditions and less than that of C when the relative humidity was below 70%. D and E took up practically no  $\text{H}_2\text{O}$ . The apparent sp. grs. in  $\text{Et}_2\text{O}$  were A 2.465, B 2.390, C 2.271, D 2.624, and E 2.685; in  $\text{H}_2\text{O}$  2.04-2.3, and in Hg 0.35-1.1.

When amorphous  $\text{SiO}_2$  was heated, the capillaries closed and the inner surfaces decreased so the  $\text{H}_2\text{O}$  absorption and the apparent sp. gr. were less. Optical examn. showed *A* and *B* were amorphous, *C* was partly, *D* mostly, and *E* entirely cryst. When quartz particles ( $<0.07$  mm.) were shaken with  $\text{C}_6\text{H}_6$  and  $\text{H}_2\text{O}$ , they immediately sank to the bottom. Amorphous  $\text{SiO}_2$  sank more slowly. When a drop of a soln. of a basic dye-stuff was added and the mixt. reshaken, the quartz went into the interface while the other  $\text{SiO}_2$  was dyed and sank.

WM. STERICKER

A simple demonstration of the effect of temperature upon a gas. C. D. HURD. *Ind. Eng. Chem.* 15, 370(1923).—If a soap film is made across the mouth of a test-tube, the change in vol. of the gas within the tube with change of temp. is shown by the formation of an expanded bubble or the withdrawal of the film into the tube.

C. C. DAVIS

The velocity distribution function and the stresses in a non-uniform rarefied monatomic gas. J. R. JONES. *Trans. Roy. Soc. (London)* 223, 1-33(1922); *Science Abstracts* 25A, 762-3.—The detn. of the distribution of the mol. velocities in the non-uniform state of a gas is in general necessary in applying the kinetic theory to the investigation of its phys. properties. Boltzmann showed that the function which expresses the law of distribution of the mol. velocities must satisfy a certain integral equation, and Enskog, in 1911, applied to this equation the method of soln. by series, and thus obtained the form of the function. He later succeeded in obtaining numerical values of the coeffs. of viscosity, heat conduction, and diffusion. The same results were obtained also by Chapman by applying Maxwell's "equation of transfer" to certain odd and even functions of the mol. velocity. Chapman and Enskog applied their methods chiefly to the case of a gas in which the mean free path of a mol. is small compared with the scale of length in which the properties of a gas vary appreciably. In the present paper the soln. is extended to gases in which this condition no longer holds. A new "equation of transfer," which is different in form from that of Maxwell, forms the basis of the method, and provides a simpler and more direct means of calcg. the rate of change of mol. properties by collision than has been used hitherto. This equation, together with Boltzmann's equation, readily provides a soln. of the distribution function to any desired degree of completeness. It was shown by Maxwell that stresses are set up in a gas by non-uniformity of temp.; in a normal gas these stresses are negligible, but in a rarefied gas this is not so, and provides a possible explanation of the phenomena of the radiometer. The investigation is here dealt with afresh by the special methods of this paper, and general formulas are obtained for the stresses. The various special mol. models discussed include centers of force varying inversely as the  $n$ th power of the distance and rigid elastic spherical mols. In the former case Maxwell's result for  $n = 5$  is confirmed, and in the latter the calcns. are carried to the third approximation, and the numerical coeff. obtained differs by 20% from that of the Maxwellian gas. A detailed comparison of the results with those of previous writers is given. H. G.

Selective interruption of molecular oscillation. ARTHUR FAIRBOURNE. *Nature* 111, 149-50(1922); cf. *C. A.* 16, 2799.—The case of a truncated cone longer than that used before is considered and it is shown that, so long as the diam. is less than the mean free path in a given gas there will be a concg. effect at the larger opening. U. S. pat. 1,414,895 by H. H. Plätt is considered to involve this principle. F. O. ANDEREGG.

Hydrogen-ion concentration and the properties of the emulsoid colloids. R. H. BOGUE. *J. Phys. Chem.* 26, 801-11(1922).—Various phys. properties of emulsoid colloids including viscosity, jelly strength, m. p. and joining strength are at a min. at a H-ion concn. corresponding to the isoelec. pt. By increasing the acidity or alkyl. from this pt. these properties rise in value. Max. ptn. of gelatin by salts takes place at the isoelec. pt. The necessity for control of H-ion concn. in investigational work on

proteins is emphasized and the desirability of a similar control in the gelatin and glue industry is pointed out; but it is not recommended that all phys. tests be made at a specified  $pH$  value.

HARRY B. WEISER

**Liesegang rings.** I. Silver chromate in gelatin and colloidal gold in silicic acid gel. II. Rhythmic bands of dyes on filter paper and cloth by evaporation. The refractivity, surface tension, conductivity, viscosity and Brownian movement of dye solutions. E. C. H. DAVIES. *J. Am. Chem. Soc.* **44**, 2698-709(1922).—Gravity decreases the rate of diffusion upward during the formation of  $Ag_2CrO_4$  bands in gelatin. Light is one of the most important variables in making bands of Au in silicic acid since no bands were formed in the dark at 0° or room temp. Rhythmic bands of 62 dyes were made on filter paper, cotton cloth and unglazed porcelain by regulated evaporation. It is probable that a film of oriented mols. precedes the formation of a band. H. B. W.

**Composition of micelles.** I. Alkali-peptized stannic acid. R. WINTGEN. *Z. physik. Chem.* **103**, 238-59(1922).—Cond. and transference measurements have been made (presumably at room temp.) with sols of stannic acid and their ultra-filtrates. The measurements are reproducible. From the results the part played by the micelle portion of the sol in conductance and transference has been calcd. Since the micelle ion behaves like an ordinary multivalent ion, an attempt has been made to apply Kohlrausch's law of the independent migration of ions to inorg. colloid-ions. In the present case the law has been found to hold. From the results of the cond. measurements, the average quant. compn. of the micelle equiv. can be calcd., i. e., the no. of mols. of  $SnO_2$  that are contained in 1 equiv. of stannic acid. The measurements indicate that a considerable portion of the alkali used for peptizing remains enclosed in the micelle. From the results of the transference measurements, the equiv.-aggregate and the quantity of enclosed alkali can be calcd. The results obtained in this way agree with those obtained from the cond. data. In consequence of the large quantity of alkali enclosed by the micelle, a decrease instead of an increase of alkali takes place at the cathode during electrolysis. The equiv.-aggregate decreases as the alkali content increases.

H. JERMAIN CREIGHTON

**Adsorption and detoxication power of certain charcoals.** G. JOACHIMOGLU. *Biochem. Z.* **134**, 493-9(1923).—Comparison of the adsorption ability of 10 samples of com. charcoals for  $I_2$  *in vitro* with the detoxicating power with respect to strychnine nitrate in the alimentary tract of the dog (*C. A.* **11**, 610). A fair degree of parallelism was shown. It was found that on the av. 0.1 g. charcoal will detoxicate 0.01 g. strychnine nitrate.

F. S. HAMMETT

**Adsorption of ions by freshly precipitated manganese dioxide.** P. B. GANGULY AND N. R. DHAR. *J. Phys. Chem.* **26**, 836-44(1922).—The coagulative power of different electrolytes, as calcd. from the adsorption of cations by  $MnO_2$ , follows the Schulze-Hardy law only partially. The effect of anions on the adsorption of cations is marked; but there is no regularity in the variations of adsorption of cations with different anions. The adsorption of ferric ions is abnormally great, probably because of decompn. of ferric salts with the formation of hydrous ferric oxide. The adsorption of elements in the same group of the periodic table is generally in the order of the at. wts.

HARRY B. WEISER

**The anomaly of strong electrolytes with special reference to the theories of J. C. Ghosh.** H. J. S. SAND. *Phil. Mag.* **45**, 281-92(1923); cf. *C. A.* **17**, 1180.—Assuming a uniform dielectric const. of the solvent for different concns. of soln. the view that solns. of electrolytes such as NaCl are practically completely dissociated is well founded. Ghosh's formulas for osmotic pressure and cond. of solns. must be considered as empirical. They cover a wide range but limits have been indicated in several directions. The statement of the subsidiary hypotheses has been modified so as to make them agree



with his mathematical formulas. Although this on the whole strengthens the theory, the no. of stated and implied subsidiary hypotheses is so great that the derivation drawn from them cannot be considered as essentially different from empirical formulas. Hindrances to cond. arising from the elec. fields due to ions in a completely dissociated electrolyte dissolved in a medium of uniform dielec. const. would be of the nature of polarization in the liquid itself. Its cond. should be greater with rapidly alternating current and under very high potential gradients than with small const. ones. Owing to the absence of these effects the idea of a solvent of uniform dielec. const. is abandoned, a conclusion previously reached by Milner on different grounds. The nature of the dielec. properties of the solvent and its role in detg. whether an ion is free or bound at a given instant have been considered and the importance of the rotational and vibrational energy of the mols. of the solvent and solvated ion has been emphasized.

S. C. LIND

Formic acid. II. Electrolytic dissociation of formic acid. FR. AUERBACH AND H. ZERLIN. *Z. physik. Chem.* 103, 178-99(1922).—In conformity with the observations of other investigators, small quantities of  $\text{HCO}_2\text{H}$  are decomposed at platinized electrodes during cond. measurements. This decompn. also takes place in solns. of  $\text{HCO}_2\text{Na}$ , bicarbonate being formed by oxidation. The cause of the oxidation is attributed to the O adsorbed by the platinized electrodes. This decompn. is prevented by treating the electrodes with H both before and during the measurements. The cond. of  $\text{HCO}_2\text{Na}$  in aq. soln. has been measured at  $18^\circ$  over the diln. range, 8-1024 l. per mol. The limiting value of the mol. cond. at infinite diln. is 91, from which the corresponding value, 362.5, has been calcd. for  $\text{HCO}_2\text{H}$ . The cond. of  $\text{HCO}_2\text{H}$  in aq. soln. has been detd. at  $18^\circ$  over the diln. range, 4-1024 l. per mol., the mol. cond. increasing from 10.16 to 126.2. This corresponds to an increase in dissoc. from 2.80 to 34.81%. The value of the dissoc. const. decreases from  $2.09 \times 10^{-4}$  at  $c = 1.000$  mol./l. to  $1.90 \times 10^{-4}$  at  $c = 0.002$  mol./l. The Ghosh theory is discussed and applied to the exptl. data. III. Partition of formic acid between water and ether and its analytical application. *Ibid* 200-37.—The partition coeff. of  $\text{HCO}_2\text{H}$  between  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$  has been detd. at  $18^\circ$  for concns. up to more than one mol./l. The coeff. of the undissociated acid is not const., but is a linear function of the concn. in the aq. phase; it varies from  $c_w/c_w = 0.395$  ( $c_w = 0.0446$  mol./l.) to 0.454 ( $c_w = 1.343$ ). The partition coeff. of the acid between  $\text{Et}_2\text{O}$  and 0.5 N  $\text{H}_2\text{SO}_4$  (the electrolytic dissoc. in the aq. phase is almost completely suppressed) has been detd. over the same concn. range. As in pure  $\text{H}_2\text{O}$ , the coeff. is a linear function of the concn. of the acid in the aq. phase. Corresponding results were obtained with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$  contg. both  $\text{H}_2\text{SO}_4$  and NaCl. The change in the value of the partition coeff. is attributed to polymerization of the acid in  $\text{Et}_2\text{O}$ . With the aid of the law of mass action the polymerization const.,  $x$ , (for the formation of double mols.) has been calcd. For  $\text{Et}_2\text{O}$  satd. with  $\text{H}_2\text{O}$ ,  $x = 0.139$ ; for  $\text{Et}_2\text{O}$  satd. with 0.5 N  $\text{H}_2\text{SO}_4$ ,  $x = 0.147$ . The true partition coeff. of the simple undissociated mols. of  $\text{HCO}_2\text{H}$  between  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$  at  $18^\circ$  is 0.393, that between 0.5 N  $\text{H}_2\text{SO}_4$  and  $\text{Et}_2\text{O}$  is 0.398, and that between  $\text{Et}_2\text{O}$  and 0.5 N  $\text{H}_2\text{SO}_4$  contg. 100 g. NaCl per l. is 0.400. The changes which take place in the vol. of the liquid phases on shaking  $\text{Et}_2\text{O}$  with 0.5 N  $\text{H}_2\text{SO}_4$  and with 0.5 N  $\text{H}_2\text{SO}_4$  contg. 100 g. NaCl per l. have been detd. With the aid of these vol. correction factors and the partition coeff., the  $\text{HCO}_2\text{H}$  concn. in the aq. soln. can be calcd., the av. error being  $\pm 0.38\%$  for 0.5 N  $\text{H}_2\text{SO}_4$  and  $\pm 0.26\%$  for 0.5 N  $\text{H}_2\text{SO}_4$  contg. 100 g. NaCl per l.

H. JERMAIN CREIGHTON

Validity of the law of mass action for ionic equilibria. J. N. BRÖNSTED AND K. PEDERSEN. *Z. physik. Chem.* 103, 307-15(1922).—The law of mass action holds for ionic reactions, provided they take place in a concd. salt soln. as solvent. This conclusion has been confirmed for the reaction,  $2\text{Fe}^{+++} + 2\text{I}^- \rightleftharpoons 2\text{Fe}^{++} + \text{I}_2$ . A conven-

ient methods described for the *detn. of soly.* in the absence of air. By means of this method the dissoc. const. of the  $I_3^-$  ion ( $I_3^- \rightleftharpoons I_2 + I^-$ ) has been found to be 0.00502 at 15.00° and 0.00540 at 18.50°.

H. JERMAIN CREIGHTON

**In-, mono-, and divariant equilibria.** XXII. F. A. H. SCHREINEMAKERS. *Proc. Acad. Sci. Amsterdam* 25, 341-53(1922).—Equations are developed concerning equil. of  $n$  components in  $n + 1$  phases when the quantity of one of the components approaches zero. The rule is deduced that when a new substance is added to an invariant equil., a monovariant equil. occurs which is represented in a  $P - T$  diagram by a curve,  $E$ ; when the new substance occurs only in one or more of the phases, which arise at the isovolumetrical reaction on addn. (withdrawal) of heat, then the temp. is lowered (raised), hence curve  $E$  proceeds from its invariant beginning point towards higher (lower) pressures. Some applications of this rule are given in detail.

E. N. BUNTING

**Catalytic reduction of carbon monoxide.** G. FESTER. *Brennstoff.-Chem.* 3, 244-5(1922).—An observation by Orlov has been confirmed (cf. *J. Russ. Phys.-Chem. Ges.* 40, 1588-90(1908)), viz., that CO when reduced at 100° by H in presence of a catalyst of Ni and Pd asbestos yields unsatd. hydrocarbons and not  $CH_4$ . The catalyst rapidly loses its activity.

J. S. C. I.

**Heterogeneous catalysis and the orientation of adsorbed molecules.** H. R. KLUYF AND C. F. VAN DUIN. *Proc. Acad. Sci. Amsterdam* 25, 324-6(1922); cf. *C. A.* 15, 3783.—In support of the theory that a positive contact catalysis can only be expected when the reacting group is turned away from the adsorbent towards the surrounding liquid, tables are given showing the increase in the rate of reaction between dihomosuccinic acid and KI caused by the addn. of 1 g. C to 100 cc. of reacting soln. The addn. of the C increases the velocity const. 300-400%.

E. N. BUNTING

**The heat of mixing of normal and associating liquids.** J. J. VAN LAAR. *Proc. Acad. Sci. Amsterdam* 25, 309-18(1922).—An exact theory is mathematically developed from which are derived the abs. values of the heat of mixing and the vol. contraction in mixing for normal liquids. The theory for associating liquids, while essentially the same, will appear in a later paper.

E. N. BUNTING

**Heat of oxidation of the alkaline earth metals.** A. GURITZ AND BENOIT. *Compt. rend.* 176, 219-20(1923).—The metals were dissolved in dil. HCl, and the heat of oxidation was calcd. from the heat of soln. of the oxide. The purity of the metal used was from 99.6% to 99.8%. The results were: Ca + O, 152.7 cal.; Sr + O, 141.8 cal.; Ba + O, 134.0 cal. The result for Ca differs by 5% from the nearest result of anyone else, and 12% from Thomson. An explanation of these discrepancies is promised.

W. P. WHITE

**Relations between the specific heats of liquids.** W. HERZ. *Z. anorg. allgem. Chem.* 125, 295-300(1923).—By taking *corresponding temps.* the relations of many properties of liquids become much simpler than when the same temp. is used for diff. liquids. Many ancient sp. ht. data are worked over on this basis, and several regularities are pointed out. Equal fractions of the crit. temp. are chosen in some cases; in others, where the crit. temps. are probably inaccurately known, the *mol. heats at the normal b. p.* are compared.

W. P. WHITE

**The dissociation of calcium sulfate at higher temperatures.** P. P. BUDNIKOV AND J. K. SYRKIN. *Chem.-Zig.* 47, 22(1923).—Dissociation begins in the neighborhood of 800°. At 1375° the dissociation pressure apparently reaches 1 atm.; melting occurs simultaneously. The decompn. products are CaO and  $SO_4$ . The results of the analysis upon the former and the differences in weight, upon heating, are given. Heating to 1000° as in the formation of *Keene's cement* produces only a small quantity (about 3.2%) of CaO.

H. C. PARKER

**The decomposition tension of fused mixtures of sodium hydroxide and zinc oxide**

and of sodium hydroxide and cadmium oxide. I. ROLLA AND R. SALANI. *Gazz. chim. ital.* 52, II, 286-313(1922).—Fe crucibles and electrodes are best for the electrolysis of fused NaOH. They are attacked up to a certain point, after which they resist by entering the passive state. Sacker (*Z. anorg. Chem.* 28, 385) detd. the conditions of this equil. and R. and S. have now detd. the effect of ZnO and CdO on it. A sheet-iron crucible is placed in a small sand bath and filled with NaOH in which an Fe wire is placed as the other electrode. On heating the bath the NaOH melts and is dehydrated. Presently the white efflorescence becomes green and gradually the whole mass becomes dark green and then permanently red-brown. This change is represented thus:  $6\text{NaOH} + 2\text{Fe} \longrightarrow \text{Fe}_2\text{O}_3 + 3\text{Na}_2\text{O} + 3\text{H}_2$  and it ceases when the Fe becomes passive. This reaction explains the difference in potential between the crucible and Fe, which is small at first, rises to 1 v. and falls to hundredths of a v. Previous workers did not det. whether  $\text{Fe}_2\text{O}_3$  is dissolved in NaOH or whether it forms a ferrate thus:  $\text{Fe}_2\text{O}_3 + 2\text{Na}_2\text{O} + 3\text{O} \longrightarrow 2\text{Na}_2\text{FeO}_4$ . At high temps.  $\text{Na}_2\text{FeO}_4$  is formed but it decomposes on cooling with sepn. of  $\text{Fe}_2\text{O}_3$ . The addition of ZnO and CdO to the NaOH has no action on the attainment of the passivity between the NaOH and the electrode material. R. and S. undertook to trace according to Lorenz (*Electrochemie geschmolzener Salze*) the polarization curves with respect to time, of the systems fused NaOH with each of the 2 oxides, and to compare them with the curve for pure fused NaOH. Observations on the decompn. tension of fused salts offer considerable difficulty. The cases here studied are not the most simple, for in the mixt. undergoing decompn. the polarization data show 4 kinds of ions sepg. at the cathode of which the decompn. tension for H and Na have relatively no interest here. The general conclusion arrived at is that the phenomena take place similarly for pure NaOH as well as for mixts. of this with ZnO and CdO. Hence the decompn. of the corresponding hydrates depends upon the decompn. tension of the ions Na, Zn, Cd (2.14, 1.80 and 0.89 v., resp.). E. J. W.

Calculations of the effective permeability and dielectric constant of a powder. G. BRETT. *Proc. Acad. Sci. Amsterdam* 25, 293-308(1922).—Since some rare substances are available only in powdered form it is desirable to know the relation between the measured and the true permeability of a powdered substance. This relation is mathematically derived. The consideration of the effects of the demagnetizing field for various models of the powder shows that to within the first-order terms the correction is the same for all models considered and may be expressed by the fact that the force on a sphere of the powder is equal to the force which would be exerted on the material if it were molded into a solid sphere. Different models give results differing only in the second-order terms in the demagnetizing field. E. N. BUNTING

Dielectric constants at the critical temperature. W. HERZ. *Z. physik. Chem.* 103, 269-72(1922).—Values for the dielec. const. at the crit. temp. (calcd. from the dielec. const. of liquids) are not alike, but show a tendency towards constancy. The same holds when the dielec. const. at the crit. temp. are calcd. from the dielec. const. of gases, although the values are often higher. H. JERMAIN CREIGHTON

The  $\epsilon$ - and  $\zeta$ -potential at the boundary barium sulfate and water. A. GYEMANT. *Z. physik. Chem.* 103, 260-8(1922); cf. C. A. 16, 1901.—The dependence of the  $\zeta$ -potential of  $\text{BaSO}_4$  on the Ba-ion concn. has been detd. by means of electroosmosis measurements. The results of the expts. indicate that to explain the  $\zeta$ -potential the adsorption of Ba ions, as well as that of all other ions present, must be taken into consideration. It has not been possible to deduce the observed dependence of  $\zeta$  on the Ba-ion concn. from that of the  $\epsilon$ -potential on this ion concn. H. J. C.

The rate of evaporation of electrons from hot filaments. W. H. RONEBUSH. *J. Am. Chem. Soc.* 45, 997-8(1923).—As a crit. test of the equation derived from statistical mechanics for the rate of evapn. (C. A. 17, 1573) calcs. are made in this note of the

rate of evapn. of electrons from a hot filament.  $E_0$ , the internal energy of evapn., is put equal to the "thermionic work function" plus the av. excess energy  $2RT$ . From this and the original equation the value of  $A$  in Richardson's empirical formula  $n = A \sqrt{T} e^{-b/T}$  is calcd. for filaments of W, Ta and Mo at 2000°K. and found to give satisfactory agreement with the values based upon Langmuir's exptl. measurements. Evidently it will be possible to calc. thermionic work functions, and hence contact potentials between metals, from thermoclec. data.

G. L. CLARK

**Photochemical kinetics.** R. WEGSCHNIDER. *Z. physik. Chem.* 103, 273-306 (1922).—A mathematical and theoretical treatment of the subject. The laws of photochem. kinetics are developed on the basis "dark-kinetics." The van't Hoff law of proportionality of chem. exchange with the absorbed light holds, provided the velocity is detd. by the photo transformation of only one mol. species in a reactive form, and also provided the spontaneous reverse transformation of the active into the inactive form may be neglected and all other partial processes of the total reaction proceed with infinite velocities. The break-down of this law for the total reaction is to be expected, provided the mol. species sensitive to light is in excess of the other species participating in the reaction. The Einstein photochem. equiv. law detd. the velocity in the van't Hoff formula or gives, at least, an upper limit for the total reaction. Thermodynamically an upper limit can be obtained at best. The following cases in which light is absorbed by one of the participants in the reaction are discussed: whether the reaction also proceeds as a "dark-reaction"; whether the opposed reaction proceeds as a "dark-reaction"; whether the entering light undergoes reflection or whether the light is also absorbed by a 2nd mol. species in a purely thermal way. Where a sensitizer is produced by the reaction, there results a continually increasing velocity, which suddenly decreases to zero after one of the participants is used up. In reality the slope of the reaction velocity is similar to that with an autocatalyst, since towards the end of the reaction the van't Hoff law is no longer valid. Equalization of differences of concn. by diffusion or convection, the spatial progress of the reaction and the monomol. reaction do not take place, if the reaction resulting from the activation of the light-sensitive mol. species does not proceed immeasurably fast and if the spontaneous inactivation of the activated light-sensitive mols. cannot be neglected. If the light is non-homogeneous then the effects of a single kind of light are to be treated as side reactions. The velocities are additive, but the total effect of heterogeneous light in finite time is usually smaller than the sum of the individual effects which different kinds of light exert alone. The effect of heterogeneous light is purely additive, only with complete absorption or with sensitizers of unchanging concn. With sensitizers which are formed during the reaction the action of non-homogeneous light can be greater than the sum of the single actions. If 2 light-sensitive mol. species participate in a reaction, it is not to be expected that the reaction velocity is proportional to the product of the quantities of absorbed light. At best, a proportionality between velocity and the 2nd or higher power of the light intensity is to be expected, provided a successive reaction requires the participation of several active mols.

H. JERMAIN CREIGHTON

**Action of heat on spherulites in helical grouping.** PAUL GAUBERT. *Compt. rend.* 175, 973-5(1922).—Though spherulites with a helical formation are in general unstable upon heating, spherulites of helenine (A), cholesterol (B), rhamnose, etc., are stable up to their m. p. Their optical properties are, however, changed. After fusion, A can be supercooled to the ordinary temp., though after some time centers of crystn. develop slowly into spherulites reaching 1 cm. diam. If crystn. is very slow, the filaments are visible with difficulty in the microscope and the compd. appears vitreous. Heated slowly, fibers become visible in a radial direction in the rings corresponding to the obtuse bisector. The series of rings corresponding to the acute bisector

show a fine granular structure. On recooling, these structural modifications persist. On beating for a long time slightly below the m. p., the granules become fibrous and also form elongated acicular crystals, both in the direction of, and oblique to the radial direction of the spherulite, owing to partial unfolding of the invisible fibers. With rise in temp. the birefringence, at first 0.20, gradually decreases and the color of the rings changes. On cooling, the optical properties become the same as before. *B* does not form nearly such perfect spherulites as *A*, and requires a higher temp. Change of temp. does not change the structure visibly and the optical properties vary little up to 130°.

C. C. DAVIS

The dedication of Sterling Chemical Laboratory. Presentation of the keys. GEO. H. CHURCH. *Ind. Eng. Chem.* 15, 462(1923). Acceptance for the university (Yale). JAMES R. ANGELL. *Ibid* 463-4. The history of chemistry in America, with special reference to Yale. EDGAR F. SMITH. *Ibid* 464-6.

E. J. C.

Separation of gas mixtures by diffusion in a flowing gas. G. HERTZ. *Proc. Acad. Sci. Amsterdam* 25, 434-41(1923).—See *C. A.* 17, 1176.

E. J. C.

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### 3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

S. C. LIND

Application of the quantum theory to the structure of the atom. I. The fundamental postulates of the quantum theory. NIELS BOHR. *Z. Physik* 13, 117-65(1923).—This is the first of a series of papers dealing systematically with the relation of the quantum theory to at. constitution. A statement and discussion of the fundamental postulates of the theory are given and its departure from the ordinary mechanical and electro-dynamical conceptions is fully discussed. It is shown that by means of the principle of correspondence the various types of transitions between stationary states can be stated in terms of the harmonic components of the motion. The stability of the stationary states of the at. systems is considered when the fields of force are conservative and also when they are non-conservative. A statement of the principle of correspondence is followed by its application to the stability of the stationary states and the nature of radiation. There is a discussion of the exchange of radiation between the atom and the electromagnetic field on the basis of the quantum theory and from the point of view of electrodynamics. The difficulties presented by reflection, dispersion and interference of light are considered. The paper is highly analytical and does not permit of a condensed abstract.

A. W. SMITH

Theory of the positive hydrogen atom. K. F. NIESSEN. *Physica* 2, 345-55(1922); cf. *C. A.* 17, 1374.—An extensive mathematical treatment of this most simple atomic structure.

R. BRUTNER

The working of new radium deposits. W. MEYERER. *Naturwissenschaften* 11, 79-80(1923).—A survey.

C. C. DAVIS

Radioactivity of potassium and of rubidium. W. E. RINGER. *Onders. physiol. Scheikunde* 1, 24-34(1921); *Physiol. Abstracts* 7, 83-4.—Earlier expts. by others, and their repetition by R., show that pure K and Rb salts are radioactive, giving off homogeneous  $\beta$ -rays. The K-rays have 10 times the penetrating power of the Rb-rays. Na and Cs are not radioactive at all, unless the Cs radiation has so little penetrating power that it escapes detection.

H. G.

Positive rays in simple gases. J. J. MCHENRY. *Phil. Mag.* (6) 45, 433-43(1923).—Expts. designed to det. the proportion of positive rays which are of at. and of mol. mass. The Thomson positive-ray app. was used. After the positive rays have received a known horizontal magnetic deflection they are deflected vertically by a known electrostatic field on to a short fixed parabolic slit. The voltage necessary is proportional to the energy of the rays. The relation between the voltage  $V$  of the electrostatic field and the

magnetic field strength  $H$  is expressed by  $V^2/H = \text{const.}$  and that between mass  $m$  and the magnetic field by  $H^2/m = \text{const.}$  for a given value of  $V$ . Preliminary expts. with  $O_2$  showed the ratio of positive rays  $O_1/O_2$  to be very variable. This was thought to be due to the presence of Hg vapor. When Hg was eliminated by a liquid-air trap  $O_1/O_2$  was about  $1/4$ ; when Hg vapor was admitted it was about 1. A tentative explanation is that a radiation emitted by the Hg causes  $O_2$  to dissociate to O. The effect was specific for O and absent in H and N. An effect which was general for all the gases examd. (O, N, H and CO) was that the ratio of mol. to at. ions increased with increasing  $V$ , which was given the following interpretation. At the lower values of  $V$  (40 v.) only the slower or low-energy ions are brought on to the slit, hence those that have fallen through a limited voltage, hence those from near the cathode. But in the cathode "dark space," which was well developed, ionization is due to collision with positive ions only, for the electrons are so close to the point of origin that they have not acquired sufficient energy to ionize. Therefore, the important conclusion is reached that shock ionization by positive ions is more likely to produce at. ions, that by electrons to produce mol. ones; or collision with a mol. ion is more energetic and hence more likely to produce dissociation. However, other possibilities suggested by the work of Aston (*C. A.* 14, 3359) are discussed. The similar behavior of  $O_2$ ,  $N_2$  and  $H_2$  indicates that the mechanism of ionization and dissociation in discharge tubes is the same for all 3, whatever it may be. Magnetic deflection of the cathode rays combined with examn. of the at. and mol. positive rays furnished further evidence that the mol. ions are formed by electronic bombardment. Mixts. of  $H_2$  and  $O_2$  in various proportions were also examd. One observation regarded as anomalous was that the hydrogen positive rays were always few in comparison with the oxygen ones and were not in proportion to the vol. of hydrogen in the tube. In a mixt. of  $2O_2$  to  $1H_2$  the positive-ray ratios  $O_1/O_2$  and  $H_1/H_2$  were found to be practically the same, so that the energy distributions are the same for the two gases; but in  $2H_2$  to  $1O_2$  the  $O_1$  ions exceed the  $O_2$  while the reverse is true of  $H_1$  and  $H_2$  ions. A few expts. with CO indicated that it is dissociated with great ease, which suggested a possible alternative explanation of the results earlier attributed to dissociation in the presence of Hg, namely, that  $O_2$  passing over stopcock grease may produce oxides of C which condense like Hg vapor in liquid air, and hence are present or absent under the same conditions as Hg, and would by dissociation furnish  $O_1$  ions without any intervention of Hg.

S. C. LIND

The question of the number of radiating atoms of various dimensions within gaseous hydrogen studied from the point of view of Bohr's atomic model. P. P. IZAREV. *Phil. Mag.* (6) 45, 430-2(1923).—On the basis of Bohr's theory of the radiation of light by the displacement of an electron from one orbit to another, the energy of 3 members of Balmer's H series, 656, 486 and  $434\mu\mu$ , representing the displacement from the 2nd to the 3rd, 4th and 5th orbits, resp., was detd. The intensities of these lines from a Geissler tube were compared photometrically with the corresponding wave lengths in a Hefner lamp, the energy distribution of which was already known. The energy of each line is thus detd. and the ratio of the no. of atoms  $N$  to the max. no.  $N_{\text{max}}$  for each type of displacement was detd. as follows:  $N/N_{\text{max}}$  is taken for  $\lambda = 656$  as 1.000, and is found for  $\lambda = 486$  to be 0.251, and for  $\lambda = 434$  to be 0.175. It is thus seen that only 25% as many displacements are from the 4th to the 2nd, and 17.5% as many from 5th to 2nd, as from 3rd to 2nd orbits.

S. C. LIND

The value of  $e/m$ . R. T. BIRGE. *Nature* 111, 287-8(1923).—B. calls attention to the fact that more detailed investigation (*C. A.* 15, 2246) leads to a probable error in the spectroscopic value of  $e/m$  (derived from the fine structure of spectral lines) of about 0.5%, an error much greater than that assumed by Paschen. The latest spectroscopic data lead to a value of 1.758 for this important const., as compared to 1.773

from deflection and Zeeman-effect data, with the probability that the latter value is the more trustworthy.

R. T. BRIGGS

**Proto-rays.** A. GÜNTHER-SCHULZE. *Z. Physik* 9, 246-50(1922).—An explanation of the abnormal gas evolution during the passage of electricity through the insulating coating which is formed upon the surface of Al, Ta, etc. when used as anodes. The max. voltage is that voltage at which positive H cations make their appearance in the gas-filled spaces of the oxide layer on the metal surface. This gas-filled space acts as a condenser and the strong field gives to the positively charged particle such a high velocity that it penetrates the electrolyte, which is the cathode, to a depth of many mols. The mols. lying in the path of the particle are disrupted as long as the kinetic energy of the particle is greater than a certain limiting value, which limiting value is different for each mol. species present in the electrolyte. The article contains practically no expl. data, these being contained in the previous article, to which this article refers. Cf. *C. A.* 17, 1370.

C. R. PARK

**Ionization by collision.** J. S. TOWNSEND. *Phil. Mag.* 45, 444-56(1923).—A general treatment of ionization by collision in elec. discharge through gases, with particular reference to that part which takes place at greater sepn. of the plates, and which is not accounted for by the simple equation applying to ionization by electronic collision. This increase of ionization at greater distances, which has always been attributed by T. to ionization by collision of positive ions, has more recently been attributed by others to different causes, such as, liberation of electrons at the negative by radiation from the body of the gas, and to liberation of electrons from the negative electrode by impact of ions. After reviewing the various claims critically, T. decides that his original theory of *ionic shock* ionization is still the most tenable.

S. C. LIND

**The element of atomic number 72.** G. URBAIN AND A. DAUVILLIER. *Nature* 111, 218(1923).—Polemical. U. and D. reaffirm their discovery of element 72, denied by Coster and Hevesy (*C. A.* 17, 1923), stating that they have examd. Zr minerals, and find the "Hf" X-ray lines to be identical with the lines of cerium previously reported by them. Whether the arc lines and the X-ray lines reported do or do not belong to the same element, in either case U. and D. claim the discovery of 72. 72 may well have the valence 4 and yet be found in rare earth mother liquors, as are Ce and Th. Cf. *C. A.* 16, 3804.

NORRIS F. HALL

**Celtium, the element of atomic number 72.** G. URBAIN. *Compt. rend.* 176, 469-70(1923).—Essentially the same priority claims as in the preceding abstr.

NORRIS F. HALL

**Hafnium and titanium.** T. E. THORPE. *Nature* 111, 252-3(1923).—Historical. The discordance in the earlier detns. of the at. wt. of Ti is probably due to the presence of an element of higher at. wt. in the preps.

NORRIS F. HALL

**The new element hafnium.** D. COSTER AND G. HEVESY. *Nature* 111, 252(1923).—The main reasons for believing that Urbain's "Celtium" is not the same as Hafnium 72, are: (1) While C. and H. have no difficulty in purifying Hf from rare earths, U. has found Ct so hard to purify that only samples of small concn. have yet been obtained, although the element was first detected in 1911. (2) Concd. Hf preps. do not show the optical spectrum ascribed by U. to Ct. (3) The X-ray spectrum of a prepn. of an element concd. enough to measure its magnetic properties should show very intense X-ray lines, not weak ones as found by D. These lines do not coincide within the error of measurement with C. and H.'s lines. C. and H. find Hf in large abundance in Zr minerals, and the Hf content of the earth's crust is estd. as  $> 10^{-3}$ . Goldschmidt and Thomsen of Christiania have found a mineral in which Hf is the main metal; this shows strong Hf X-ray lines. Dr. Scott's preps. show no Hf lines (cf. following abstr.). The discovery of Hf was guided by Bohr's theory.

NORRIS F. HALL



Isolation of the oxide of a new element. ALEXANDER SCOTT. *J. Chem. Soc.* 123, 311-2(1923).—Oxide preps. made from a black titaniferous iron sand from New Zealand showed an at. wt. of 144 in preliminary detns. The prep. is submitted to C. and H. for analysis with the result indicated in the preceding abstr. N. F. H.

The K absorption spectrum of the element 72 (celtium). M. DE BROGLIE AND J. CARRERA. *Compt. rend.* 176, 433-4(1923).—Several specimens contg. Zr have been examd. and a feeble but clear absorption band of  $\lambda = 0.1905 \text{ \AA}$ . is found. This is certainly to be ascribed to 72, of which the specimens contain several %. N. F. H.

The high frequency spectrum of celtium. A. DAUVILLIER. *Compt. rend.* 176, 676-9(1923).—D. admits a discordance between his values (*C. A.* 16, 2638) for the lines  $L\alpha_1$  and  $\beta_1$  of Ct, and the most probable values obtained by interpolation, but states the discordance to be within the exptl. error. Redetns. with improved technic now show  $L\alpha_1 = 1564 \text{ \AA}$ ,  $L\beta_1 = 1323 \text{ \AA}$ . (cf. Coster and Hevesy 1565.5 and 1323.7). The lines cannot be higher order lines of any other element. The line  $\beta_1$  is now obtained and has a  $\lambda = 1373 \text{ \AA}$ . (cf. C. and H., 1371.4). U. and D. insist that a trace of element 72 was proved to be present in Urbain's sample in their first publication and that therefore they are the discoverers.

NORRIS F. HALL

The optical spectrum of hafnium. H. M. HANSEN AND S. WERNER. *Nature* 111, 322(1923).—Fifty-two lines ascribed to Hf are reported, with wave lengths to hundredths of an  $\text{\AA}$ ., and relative intensities. These all lie in the region 2500-3500  $\text{\AA}$ . Not the slightest trace of any of the lines reported by Urbain as belonging to Ct appears on the plates. Preps. initially contaminated by rare earths were obtained spectroscopically free from all elements except Hf, Zr, and Ti. Many of the Hf lines have been previously ascribed to Zr.

NORRIS F. HALL

Continuous Röntgen spectra. H. KULENKAMPPF. *Ann. Physik* 69, 548-96 (1922).—The intensity and spectral distribution of continuous Röntgen radiation were investigated, as dependent on the ordinal no.  $Z$  of the anticathode metal and on the voltage  $V$  of the cathode rays. The exptl. arrangements were: a discharge tube with Al window and a revolving 4-cornered anticathode, const. storage-battery voltage, a Bragg spectrometer with calcite crystal, and an air-filled ionization chamber for the intensity measurements. The cathode-ray energy was measured by the heating effect produced at the anticathode, a thermocouple being used. The Röntgen rays were observed always at right angles to the cathode rays. The  $Z$ -dependence was detd. for Al, Fe, Ca, Ni, Cu, Ag, Sn, and Pt, at 10,470 v. The dependence on potential was detd. for Ag and Pt for the interval 7000 to 12000 v. Altogether the wave-length region from 1.0 to 2.8  $\text{\AA}$ . was covered. The observed spectral intensity is noticeably dependent on various factors, of which the following were ascertained: (a) the amt. of absorption which the Röntgen rays undergo inside the anticathode was detd. by changing the angle which the cone of Röntgen rays made with the surface of the anticathode, (b) measurements were made also of the absorption of the rays in the Al window of the tube and in the air traversed, and of the reflecting power of the crystal as dependent on wave length (cf. *C. A.* 17, 237). Making corrections for these effects, K. obtains the true distribution of intensity, as measured by the ionization produced. The Röntgen ray intensity ( $J_r$ ) plotted against frequency ( $V$ ) indicates a direct proportionality of  $J_r$  with  $(v - v_0)$ . The tangent of the slope of the straight line is proportional to  $Z$ . Changing the voltage (with  $Z$  const.) gives a series of parallel straight lines. In the neighborhood of the limiting frequency there appears a noticeable deviation from the straight line, a matter which is fully discussed. These results may be expressed by the simple empirical formula  $J_r = C\{Z(v_0 - v) + Z^{\frac{1}{2}}\}$  in which  $C$  and  $b$  are const. and  $v_0$  is a function of the voltage.

R. T. BIRGE

Continuous Röntgen spectra. E. WAGNER AND H. KULENKAMPPF. *Physik. Z.* 23, 503-6(1922).—See preceding abstr.

R. T. BIRGE

**Determination of the coefficient of reflection of X-rays for calcite and rock salt.** BERGEN DAVIS AND H. M. TERRILL. *Phil. Mag.* 45, 463-70(1923).—An examn. of the intensity of the reflection of X-rays from calcite and rock salt by placing two faces parallel and reflecting the beam from the first on to the second and then into an ionization chamber. Max. reflection is obtained when the two surfaces are exactly parallel. By turning the second through slight angles in either direction, intensity curves were obtained called "rocking curves." The app. was so arranged that the second crystal could be removed, allowing the radiation reflected from the first to pass directly into the ionization chamber, thus furnishing a direct ratio of the two intensities; this was called the % of reflectivity. Three pairs of calcite and two pairs of rock-salt crystals were measured and compared with the results of other observers. The reflectivity was found to be highly dependent on the perfection and polish of the crystal surface. It is not possible to give a simple definition of reflectivity as some have attempted. On the "rocking curves" with intensity of reflection as ordinates and angles away from the parallel as abscissas, the rougher surfaces give broader curves with greater area, while the highly polished surfaces give high curves of great intensity but narrow and of smaller area, therefore of greater intensity but of less total reflecting power. Rock salt and calcite cannot be directly compared; the former is always less perfect and gives a curve of the low broad type. For the more perfect crystals the reflectivity increases with wave length of the radiation, while the opposite is true for the less perfect ones. Cf. *C. A.* 16, 3809.

S. C. LIND

**Series in the lead arc spectrum.** V. THORSEN. *Naturwissenschaften* 11, 78-9 (1923).—Preliminary data are given of a no. of new lines in the Pb arc spectrum, which are soon to be published in greater detail elsewhere. From these a sharp and a diffuse series could be detd., which together comprise approx.  $\frac{1}{3}$  of the known spectrum. The lines were observed by a Hilger quartz spectrograph with the source of light an arc light with its positive electrode a Cu plate on which is a piece of Pb, and its negative electrode a pointed Cu rod. An intense Pb arc is obtained at 220 v. and 2 amp. With the 10 triplets of Kayser and Runge and the 4 of Eder and Valentas were found 20 Pb lines which, in combination with previously known lines, give 12 new triplets.

C. C. DAVIS

**High-frequency spectra: K-series of platinum.** J. S. ROGERS. *Proc. Roy. Soc. Victoria* 34, 196-206(1922); *Science Abstracts* 25A, 758.—A description is given of an accurate method of measuring the wave lengths of the X-ray spectrum of Pt. The following mean values are expressed in Å. units:  $Pt\alpha_1$  0.1895  $\pm$  2,  $Pt\alpha_2$  0.1851  $\pm$  1,  $Pt\beta$  0.1644  $\pm$  2,  $Pt\gamma$  0.1596  $\pm$  2,  $W\gamma$  0.1794  $\pm$  2.

H. G.

**The explosion spectra of the alkaline earth metals.** R. A. SAWYER AND A. L. BECKER. *Astrophys. J.* 57, 98-113(1923).—A modification of Anderson's (*C. A.* 14, 3195) exploded wire as a source of light is developed, in which there is exploded, in place of the wire, an aq. soln. of any salt of the desired metal. The soln. is held by an asbestos fiber which is uninjured by the explosion and may be used repeatedly. The explosion spectra of chlorides of Ba, Ca, Mg, and Sr were photographed between 2280 and 4550 Å. Except lines due to impurities, the spectra thus produced are almost pure spark spectra, consisting chiefly of doublets in the subordinate series. Resonance lines of the arc spectra appear with diminished intensity. These data are thought to support, at least qualitatively, Sommerfeld's displacement law and Saha's theory of ionization by high temp.

W. P. MEGGERS

**Vacuum arc for extended spectra extending from visible light to soft X-rays.** H. NAGAOKA AND Y. SUGIURA. *Astrophys. J.* 57, 86-91(1923).—A modified type of arc is described which with 2 to 5.5 amp. at from 80 to 150 v., is an intense source of very sharp lines. The cathode is a C rod covered with a layer of oxides of Ba and Sr and

sheathed in a silica tube; the anode consists of the metal or salt to be tested, placed in another silica tube. These tubes are fastened in necks of a vacuum flask and light is excited by cathode bombardment after a glow discharge is started with an induction coil. The tendency of metal to deposit on the walls or window, the necessity of renewing the oxide layer on the cathode, the comparatively short life of the arc, besides the need of water-cooling and continuous pumping are mentioned as some of the inconveniences but these are offset by the production of sharp spectral lines free from pressure and electric-field effects. When the potential was raised to 1500 v., rays were emitted which affected a photographic plate covered with Al foil placed within the flask. These are thought to be soft X-rays.

W. F. MEGGERS

The rare earths. XIII. Studies in the absorption spectra. I. F. YNTEMA. *J. Am. Chem. Soc.* 45, 907-15(1923).—To obtain data under uniform conditions the visible absorption spectra of Pr, Nd, Sm, Eu, Dy, Ho, Er, and Tm were measured at various concns. and thicknesses of soln. by a photographic method. The results are given in graphs and tables contg. the wave lengths of the max. of each band, the depth of layer, the normality at which the band last appears, and the equiv. thickness of the last appearance. A method for the quant. estn. of rare earths is outlined. Periodic relations among the absorption bands were looked for but no very definite relations were found. Cf. Herzfeld, *C. A.* 16, 682.

W. F. MEGGERS

The structure of the band spectrum of hydrogen. MASAZO KIYUI. *Proc. Phys.-Math. Soc. Japan* 5, 9-17(1923).—According to recent theoretical works on band spectra a "band" consists of 3 series of lines, viz., the positive, null, and negative branches, which correspond, resp., to decrease, no change, and increase of the angular momentum of the mol. by one or several quanta, during the change of the mol. configuration causing the radiation. The wave-numbers of the lines of each series are represented by a parabolic formula in quantum no.  $M$ . In the present expt. with arc discharge in H, K. obtained a spectrum somewhat different from the ordinary H spectrum with vacuum discharge, and selecting strong lines in the orange region of the spectrum he sorted out a series of 7 members which can be represented by the formula  $\nu = 17206.28 - 6.8052 m^2$ . This series is to be considered as connected with the Fulcher (*Astrophys. J.* 37, 60(1913)) bands in that this series corresponds to the null branch, and the Fulcher bands to the positive and negative branches of a complete band. Appropriate formulas are given for the Fulcher bands, and from the coeff. of  $m$  the moment of inertia of the H mol. is calcd. as  $1.7 \times 10^{-4}$  (c. g.). From this the distance of the nuclei in the H mol. is calcd. as  $46 \times 10^{-9}$  cm., which is a somewhat smaller value than that given by the Bohr-Debye model.

W. F. MEGGERS

The effect of a probable electric field on the bands of nitrogen. SNEJAMOY DATTA. *Astrophys. J.* 57, 114-20(1923).—Broadening of N positive bands in the presence of Br vapor was observed when the partial pressure of Br vapor in a discharge tube contg. some air was varied by immersing a side tube in different freezing mixts. With the lowest partial pressure ( $-78^\circ$ ), the bands were sharp, but as the pressure was raised the bands showed evidence of blurring, especially the more refrangible ones, the effect increasing with the pressure until for  $-5^\circ$  even the heads had disappeared, leaving only diffuse patches where the bands had been. The blurring may be a Stark effect produced by the elec. fields of the ionized Br atoms. Though this effect has not been directly observed in the lab., it was predicted by Hettner from theoretical considerations. The similar blurring due to increased pressure in pure N may also be a Stark effect. However, the cyanogen band was unaffected by the Br. The displacements observed by Dufour and Clinkscales in the case of the Br and Na bands may also be a Stark effect due to the elec. field of the ionized atoms of the foreign gas, even though the effect has not yet been observed for any bands in the lab.

W. F. MEGGERS

**The Stark effect on the secondary spectrum of hydrogen.** MASAZO KIUTI. *Japan. J. Physics* 1, 29-39(1923).—By the method first used by Lo Surdo, the Stark effect on the lines of the secondary spectrum of H in the region between  $H_{\alpha}$  and  $H_{\beta}$ , including the Fulcher bands, was investigated. A max. field of 80,000 to 110,000 v./cm. was produced in front of the cathode of a discharge tube with terminal voltage 4,000 to 6,000 v., the bore of the capillary into which the cathode was fitted being about 1 mm. The pressure in the tube was kept const. at about 2 mm. length of Crookes dark space, by continual evacuation and admittance of the gas. With the dispersion  $31 \text{ \AA./mm.}$ , which was obtained by the use of a plane grating, over 100 lines in the region showed measurable effects. They are either displaced on one side, toward the red in most cases, or sepd. in an asymmetrical manner. The amt. of displacement seems to increase more rapidly than the field intensity, if it is not proportional to the latter. Largely affected lines are situated rather closely in groups, but contrary to expectation no simple rule was found for the Stark effect on the Fulcher bands. The numerical results are given in tables. W. F. MEGGERS

**Inhibition of the photochemical decomposition of hydrogen peroxide solutions.** I. WM. T. ANDERSON AND H. S. TAYLOR. *J. Am. Chem. Soc.* 45, 650-62(1923).—The inhibitory effects of 25 typical org. compds. on the photochem. decompn. of  $H_2O_2$  solns. have been studied in 4 definite spectral regions of the ultra-violet. The inhibition of such agents has been associated with the absorptive capacity of the org. compds. for ultra-violet light. A striking correlation between these two factors has been obtained in the case of  $C_6H_6$ , several esters, acids, amides, ketones and alkaloids. The retarding action of amines and alcs. requires an explanation based on other causes than absorption. It has been shown that the inhibitors act more efficiently when in  $H_2O_2$  soln. than when in a screening soln. of similar thickness and concn. A possible reason for this is advanced. E. P. WIGHTMAN

Spectroscopic methods of analytical chemistry (AUER-WELSCH) 7. Photochemical kinetics (WEGSCHNEIDER) 2. Absorption spectra of pyrrole and its derivatives (KORSCHUN, ROLL) 10.

BOUTARIC, A.: *La vie des atomes*. Paris: Ernest Flammarion. Fr. 7.50.

PASCHEN, F. and GÖTZE, R.: *Seriengesetze der Linienspektren*. Berlin: Julius Springer. 154 pp.

SOMMERFELD, A.: *La constitution de l'atome et les raies spectrales*. Paris: Albert Blanchard. 384 pp.

#### 4—ELECTROCHEMISTRY

COLIN G. FINK

**Heating electric steel furnaces.** M. GILLOT AND V. GUILLERMIN. *Rev. ind. minerale* 1, 249-57(1921); *Rev. metal.* 18, 590.—Furnaces give the best results with a surface of bath not over  $1.20 \text{ m.}^2$  per electrode for small furnaces and  $1.80 \text{ m.}^2$  for 15-ton furnaces. The output per electrode should be not over 3-4 amp. per  $\text{cm.}^2$  for carbon and 12 for graphite. Various little known methods are described for economizing heat by prevention of leakage, better conduction and convection within the furnace, and construction of electrodes. C. C. DAVIS

**Formation of ferrosilicon in carbide works.** O. HACKL. *Chem.-Ztg.* 46, 740(1922).—In the manuf. of  $\text{CaC}_2$  at Austrian and Bavarian works a no. of brittle metallic reguli were obtained which proved to be ferrosilicon contg. a high % of Si. J. S. C. I.

**Use of granulated nickel for electric heating.** O. DONY-HÉNAULT. *Bull. acad.*

roy. Belg. 8, 67-70(1922).—"Mond" Ni is suitable for use in place of steel in the construction of resistances used in elec. furnaces. The thin black layer of oxide with which the Ni becomes coated when heated is a conductor when cold. The following results give the resp. percentage increases of wt. due to oxidation when steel and "Mond" Ni spheres of the same size were maintained for long periods at a red or a white heat. Percentage increase of wt. after 20 hrs. at 600-700°, steel 2.77, Ni 0.113%; after a further 17 hrs. at 1000°, steel 9.40, Ni 0.73%.

J. S. C. I.

Electrodeposition of copper. W. E. HUGHES. *Beams* 12, 92-5(1923); cf. C. A. 17, 930.—The acid sulfate Cu hath, although simple in compn., has been much investigated. There is still a difference of opinion as to the exact electrode reactions. The discussion of the electrode reactions as given below from the view-point of the electron theory, is considered of great value to the practical operator. At the cathode,  $\text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu}$ . This means that in  $\text{CuSO}_4$  soln., the Cu ion is deficient of 2 electrons, and hence 2 electrons pass to it from the cathode. This makes the ion electrically neutral, and Cu atoms deposit on the cathode. At the anode,  $(\text{SO}_4)^{--} - 2\text{e}^- \rightarrow (\text{SO}_4)$ . This means that the  $(\text{SO}_4)$  ion has 2 electrons to spare, and hence 2 electrons pass from it to the anode. This leaves the sulfate radical free to act on the anodic Cu as shown in equation (4-a). Sometimes secondary cathodic reactions take place as follows: (2)  $\text{Cu}^{++} + \text{e}^- \rightarrow \text{Cu}^+$ , and (3)  $\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$ . This is a transition from cupric ( $\text{Cu}^{++}$ ) ions to cuprous ions, and finally to Cu atoms, which are electrically neutral. The action of the sulfate radical in attacking and dissolving the anodic Cu is as follows: (4-a).  $\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{++}$ . This means that the sulfate radical acts on the Cu atom of the anode, dissolves it, and brings it into a medium in which the two are again sep'd. by the  $\text{H}_2\text{O}$  mols. There are now 2 parts of a mol., each charged because of sep'n., the Cu has lost 2 electrons, and the  $\text{SO}_4$  has gained 2. Sometimes the cuprous ion is first formed, to change into the cupric ion later on, as follows, (4-b)  $\text{Cu} - \text{e}^- \rightarrow \text{Cu}^+$ , and (4-c),  $\text{Cu}^+ - \text{e}^- \rightarrow \text{Cu}^{++}$ .

CHAS. H. ELDRIDGE

Relation between current, voltage, and the length of carbon arcs. A. E. R. WESTMAN. *Trans. Am. Electrochem. Soc.* 43, preprint (May, 1923). C. H. ELDRIDGE

The Estelle process. (Leaching sulfide ores.) AXEL ESTELLE. *Can. Mining J.* 43, 672-5; *Iron & Steel Can.* 5, 187-90(1922).—The similarity of the Eustis process of electrolytic production of Fe from its ores (cf. *Mining Met.* No. 180, 17; C. A. 16, 4143) to the Estelle patents (cf. C. A. 10, 168) is discussed. Direct leaching of sulfide ore, even when the Fe is present as  $\text{FeS}$ , with  $\text{FeCl}_2$  soln. is difficult in operation, on account of interference by the pptd. S, hydrolysis of the Fe, formation of sulfates, and soln. of other metals. The Estelle process avoids these difficulties, leaching first with weak non-oxidizing acid (preferably  $\text{HCl}$ ). The resulting  $\text{FeCl}_2$  is electrolyzed in simple cells with insol. anodes; a portion of the Fe is deposited and the remainder converted to  $\text{FeCl}_3$ . The latter is passed into an absorption tower with the  $\text{H}_2\text{S}$  evolved in the first leaching, which regenerates  $\text{HCl}$ , forming more  $\text{FeCl}_2$  and liberating free S in an easily recoverable form. Sulfides of other valuable metals in the ore are left behind in the leaching and are recovered in a sep. process. E. describes also a process of electrolytic reduction of Fe oxides, using a hot slimy ppt. of  $\text{Fe}(\text{OH})_3$  suspended in concd.  $\text{NaOH}$  as electrolyte. The  $\text{Fe}(\text{OH})_3$  is decomposed, depositing Fe on the cathode in a smooth layer, liberating  $\text{O}_2$  and  $\text{H}_2\text{O}$ , while the  $\text{NaOH}$  is unchanged. No diaphragms are required. The Fe oxides must be first hydrated, which can be done practically with  $\text{NaOH}$  or  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{O}$ . The cells may be made air-tight and the  $\text{O}_2$  collected.

A. BUTTS

Oxygen overvoltage of artificial magnetite in chlorate solutions. H. C. HOWARD. *Trans. Am. Electrochem. Soc.* 43, preprint (1923).—The O overvoltage on magnetite in  $\text{N NaClO}_3$  was found to be 0.4 to 0.6 v. lower than on smooth Pt, depending on the

c. d. This fact is given as the probable explanation for the non-production of perchlorate at a magnetite anode. M. KNOBEL

**Effect of current density on overvoltage.** M. KNOBEL, P. CAFLAN AND E. EISESMAN. *Trans. Am. Electrochem. Soc.* 43, preprint (1923).—Values of overvoltages of  $H_2$ ,  $O_2$ ,  $Cl_2$ ,  $Br_2$ , and  $I_2$  were made on all the more common metals and alloys at c. ds. varying from 0.001 to 0.5 amp. per sq. cm. at  $25^\circ$ . Comprehensive tables and curves show findings. Correct results are given by the method using a reference electrode with small glass tip pressed against the active electrode. The general form of  $H_2$  overvoltage curve is similar to that of a logarithmic curve.  $Pb$ ,  $Hg$ , and  $Cd$  rise rapidly to a high overvoltage at low c. ds. and show but little further change. Metals generally specified as of "low overvoltage," such as  $Cu$  and  $Au$ , show a more gradual increase of overvoltage with current, but in general ( $Pt$  and  $Au$  excepted), finally attain values as high as "high-overvoltage" metals. Max. value found for  $H_2$  overvoltage = 1.30. Platinized  $Pt$  maintains low overvoltage values; even at 14 amp. per sq. cm. the value is only 0.50 v. No generalizations of importance can be given for the halogens, except that graphite shows max value and platinized  $Pt$  the min. value.  $O_2$  overvoltages are less reliable than either  $H_2$  or halogen values.  $H_2$  overvoltages were detd. in 2 N  $H_2SO_4$ ;  $O_2$  values in N KOH; Na or K halide was used for halogen overvoltage. C. H. E.

**New type of copper oxide cell.** M. LEBLANC, JR. *Bull. soc. franç. élec.* [4] 1, 427-34 (1921); *Science Abstracts* 25B, 540.—After describing the characteristics of the well known Cu oxide cell and comparing this with the Leclanché type L, describes a new model which is made by the Hewittie Elec. Co. It consists of a cylinder of Cu oxide on which is wound an open spiral of Cu wire. It is stated that the reduced Cu can be re-oxidized satisfactorily, whereas in some previous cases the agglomerate became powdery after re-oxidation by heating. H. G.

**Complete million-volt laboratory.** J. F. PETERS AND D. F. MINER. *Elec. World* 81, 791-4 (1923).—An illus. account of a thoroughly equipped exptl. station of the Westinghouse Co. devoted exclusively to research problems in the use of very high voltages. C. G. F.

**A practical neon night lamp.** LOUIS BELL. *Elec. World* 81, 751 (1923).—Detailed description of a small Ne lamp that will operate on 110-volt circuits. C. G. F.

The decomposition tension of fused mixtures of sodium hydroxide and zinc oxide and of sodium hydroxide and cadmium oxide (ROLLA, SALINI) 2. Roofing sheets (U. S. pat. 1,449,058) 20.

EYDOUX, DENIS and LAURENT, JÉRAN: L'usine hydro-électrique de Saint-Lary, de la Société minière et métallurgique de Penarroya. Paris: Revue Industrielle, 55 pp.

Lehrbuch der Elektrotechnik. Edited by K. Esselborn. Leipzig: Wihl. Engelmann, 753 pp.

LEVY, S. L.: Incandescent Lighting. London: Pitman, 138 pp. 3s.

RUSS, EMIL FR.: Die Elektrometallöfen unter bes. Berücks. d. Öfen zum Schmelzen von Kupfer u. Kupferlegierungen. Munich & Berlin: R. Oldenbourg. 161 pp. M 7.50, bound 9.30.

**Primary battery.** E. H. BECKER. U. S. 1,450,059, Mar. 27. A mech. device is provided for automatically adding new material or sounding a warning signal as the positive element of the battery is consumed by the electrolyte.

**Primary battery.** M. L. MARTUS, J. G. ROSS and E. H. BECKER. U. S. 1,450,043, Mar. 27. Structural features.

**Storage battery.** W. H. EBLEY and G. H. HANDASYDE. U. S. 1,449,746, Mar. 27. Structural features.

**Storage battery.** W. P. LOUDON. U. S. 1,449,825, Mar. 27. Structural features.

**Storage battery.** N. B. LAING and F. C. RINDFLISH. U. S. 1,450,889, Apr. 3. Structural features.

**Storage battery.** A. H. WILLIAMS. U. S. 1,450,533, Apr. 3. The negative plate grids are filled with electrically refined homogeneous, pure fibrous sponge Pb united to the grid by a film of pure Pb in integral union with both materials.

**Storage battery plate of tubular type.** E. W. SMITH. U. S. 1,450,565, Apr. 3. Rubber slotted tubes are protected by asbestos paper lining from injurious action of active material within the tubes.

**Storage battery testing device.** J. W. MARTIN. U. S. 1,448,142, Mar. 13. The device is adapted for use on automobiles. It comprises an electrolyte hydrometer box to which electrolyte is drawn for testing by suction from the engine intake manifold.

**Regenerating lead storage batteries.** H. O. PARKER. U. S. 1,449,833, Mar. 27. The acid is removed from the battery and it is repeatedly washed out with  $H_2O$  and allowed to stand between washings, filled with a 5% KOH soln. in  $H_2O$ , repeatedly electrolyzed in this soln. and again washed out.

**Accumulator electrodes.** JIRO YOKOYAMA and HATSUJIRO MAKINO. Japan. 40,465, Oct. 28, 1921. A melted mixt. of Pb 100 and powdered S 30 at 400-500° F., is poured into a mold to form a plate having troughs along the both sides. Two pairs of them are immersed in  $H_2SO_4$  of 25° Bé; and an elec. current is passed for about 40 hrs. until the color of the anode becomes light brown and that of the cathode deep gray. Then the troughs are filled with asbestos and packed with the same material for the electrode.

**Accumulator electrode.** YOSHITARO OKAZAKI. Japan. 40,437, Oct. 26, 1921. The electrode, manuf. as usual, is immersed in  $H_2O$  and an elec. current is passed until the plate is no longer acid. Then it is dried *in vacuo* or in  $N_2$ . A cell constructed from these plates can be used at once without charging.

**Galvanic battery electrode.** M. L. MARTUS. U. S. 1,450,004, Mar. 27. A mixt. of Cu oxide and NaOH is molded and baked in an atm. impregnated with powd. Zn sufficient to form a deposit of Zn on the outer surface of the electrode which prevents premature corrosion.

**Purifying manganiferous material.** H. DE OLANETA. U. S. 1,448,110, Mar. 13. Impurities are removed from  $MnO_2$  for batteries or similar material by the action of  $NH_4Cl$ .

**Electric-furnace production of iron or steel.** A. E. GREENE. U. S. 1,449,094, Mar. 20. A ferrous metal charge is placed in an elec. furnace having an acid lining, C is added to the charge and a slag is then formed comprising a non-ferrous basic slag-forming material such as lime and  $SiO_2$ , beneath which the metal is subjected to reducing action.

**Electric arc furnace for melting metals.** L. TAGLIAFERRI. U. S. 1,449,307, Mar. 20. Different sets of electrodes are so mounted in the furnace that arcs may be produced either between the 2 sets of electrodes above the metal bath or one set of electrodes and the metal carried by the body of the furnace.

**Automatic electric regulating devices for arc furnaces.** R. D. EVANS. U. S. 1,449,593, Mar. 27.

**Automatic feed for electric arc furnace electrodes.** J. A. SERDE. U. S. 1,449,251, Mar. 20.

**Rotating or oscillating electric furnace plant.** A. H. PERHSON. U. S. 1,449,834, Mar. 27. A drum-shaped elec. furnace is mounted on a common axis with another

treating chamber, *e. g.*, a preheating and reducing chamber employing ore-reducing gases from the elec. furnace.

**Apparatus for moving electrodes of electric furnaces.** W. DYRSSEN. U. S. 1,450,668, Apr. 9. Differential gearing is provided between a const.-speed elec. motor and the electrode to regulate the feed of the latter.

**Electrical resistance.** F. HOBSON. U. S. 1,450,725, Apr. 3. A coil of C is used as a resistance unit for elec.-furnace heating elements.

**Electric-furnace resistor.** O. A. COLBY. U. S. 1,448,388, Mar. 13. Dished refractory elec.-cond. members contg. granular resistor material are supported under compression in the furnace chamber and constitute the resistor. The dished members and granules may both be formed of carbonaceous material.

**Electric resistance furnace.** E. A. A. GRÖNWALL. U. S. 1,450,543, Apr. 3. Pipes of carbonundum or other refractory material contain carboniferous auxiliary resistance material to which current is supplied from hollow electrodes.

**Electrolysis of water.** R. PECHERANZ. U. S. 1,448,037, Mar. 13. In a  $H_2O$ -decomp. app. of the filter-press type, electrodes are formed of thin sheet metal with thin partitions of pure Ni between the electrodes. The partitions are provided with extremely minute perforations over substantially their entire surface. Cf. C. A. 17, 603.

**Electrolytic recovery of copper.** G. D. VAN ARSDALE. U. S. 1,449,462, Mar. 27. A mass of cement Cu is introduced into an electrolytic cell in electroconductive contact with an anode of Pb or graphite or other material which remains insol. during the electrolysis and the cement Cu is replenished as transformed in the cell.

**Reducing "chromium group" trioxides to lower oxides.** R. E. PEARSON and E. N. CRAIG. U. S. 1,448,036, Mar. 13. See Can. 221,041 (C. A. 16, 3267).

**Master phonograph records.** W. H. COLE. U. S. 1,448,792, Mar. 20. Metal, *e. g.* Ag, is directly deposited on the face of a wax record by applying a soln. of salts of the metal, *e. g.*, ammonical  $AgNO_3$ , and alc. and pptg. with  $CH_3O$ . Additional metal, *e. g.*, Cu, is then electrolytically deposited.

**Electrode for electrolyzing caustic soda (for sodium production) or other fused materials.** T. KOLKIN. U. S. 1,449,008, Mar. 20. The electrodes are grooved so as to permit the mounting of gauze net and close spacing of the electrodes for obtainment of suitable current d. without increasing the usual voltage.

**Electrolytic cell adapted for hypochlorite production.** J. GERSTLE. U. S. 1,448,208, Mar. 13. Structural features. The cathode is strung with Ag wire.

**Electrolytic apparatus.** J. N. SMITH. U. S. 1,450,156, Mar. 27. The app. is adapted for decomposing  $H_2O$ , saline solns. or for depositing metals. It comprises electrode couples each consisting of a pair of opposed tubular electrodes operatively spaced apart and an electrolyte supply chamber common to all the couples. Each of the electrodes affords communication between the interior and exterior of the electrolyte chamber.

**Rotating apparatus in the electrolytic bath.** SEIZABURO YUNOKI. Japan. 40,410, Oct. 25, 1921. App. for rotating the cathode in the manuf. of Cu plates or tubes is specified. Cf. C. A. 16, 28.

**Electroplating with tin.** ZENJI SUGAWARA. Japan. 40,360, Oct. 19, 1921. Addn. to 37,221 (C. A. 15, 3594). The electrolyte consists of 30 g.  $Al(OH)_3$  and 30 g. boric acid added to an aq. soln. of Na stannate and made to 1 l. with  $H_2O$ ; to this 5 g. of glycerol is added. The upper clear soln. is used with an e. m. f. of 5 v. The method is also applicable for a mixed soln. of Pb and Sn salts. The amt. of stannate is not given.



## 5—PHOTOGRAPHY

It is with deep regret that we announce the death, on May 11th, of Dr. Louis Derr, who has served faithfully and well as Assistant Editor of *Chemical Abstracts* in charge of this section since the early days of the journal. In addition to his editorial work Dr. Derr did a large part of the abstracting in his field. By his death, which followed an illness of five weeks, the Journal has sustained a great loss. It would be difficult to overestimate the value of the unselfish service which Dr. Derr rendered during his long connection with Chemical Abstracts.

## 6—INORGANIC CHEMISTRY

H. I. SCHLESINGER

The properties of phosphorus. ALFRED STOCK. *Z. anorg. allgem. Chem.* **125**, 223-34 (1923).—A criticism of an article by W. Marckwald and K. Helmholz (*C. A.* **17**, 17), especially of their statement that red (or violet) phosphorus melts at  $592.5^\circ \pm 0.5^\circ$  and of their interpretation of a lecture expt. by S. and a modification of the same by M. and H. The m. p. of the P is materially influenced by the rapidity of heating, prior treatment, etc. S. explains how the behavior of the P in these expts. may still be accounted for by his assumption of the existence of several modifications of P.

H. C. PARKER

Active hydrogen. Its preparation from metallic hydrides. Y. VENKATARAMAIAH. *Proc. Science Assoc. Maharajah's College, Vizianagram*, Dec. 1922, 6-9; cf. *C. A.* **17**, 1175.—Active H was prepd. by the action of  $H_2O$  and by heat on metallic hydrides and by the action of H on fused metals. (1) *Decompn. of NaH, of KH and of CaH<sub>2</sub> by heat.*—Pure Na, K, or Ca was satd. at  $200^\circ$  with H and the temp. then raised until gas was liberated. This gas was cooled by ice, passed over powdered S and then over paper wet with  $Pb(OAc)_2$ . After 2 hrs. the latter turned black. (2) *Action of H on fused Na, K and Ca.*—Na, K or Ca at  $670^\circ$  treated with dry H gave a gas which blackened  $Pb(OAc)_2$  paper in 30 min. (3) *Decompn. of NaH by  $H_2O$ .*—Na at  $380^\circ$  treated with dry H, the NaH condensed and decompd. by  $H_2O$  satd. with H and the gas passed over S, blackened  $Pb(OAc)_2$  paper in 4 hrs. It is inferred that  $H_2$  was formed in all cases. The app. is illustrated.

C. C. DAVIS

Action of hydrogen sulfide on lead peroxide. M. V. N. SWAMY AND V. SIMHACHETAM. *Proc. Sci. Assoc. Maharajah's College, Vizianagram*, Dec. 1922, 17-21.—A study of the reaction products of the action of  $H_2S$  on  $PbO_2$  and the conditions influencing the reaction. *Pure  $PbO_2$*  (98.6%). With  $H_2S$  dild. with 5 times its own vol. of air, the reaction with  $PbO_2$  does not take place at 0.125, 0.25, 0.5 or 1.0 atm. pressure, but the dark brown  $PbO_2$  becomes light brick red. Even if the concn. of  $H_2S$  is increased, or if its pressure is increased to 2.5 atm. or if the  $PbO_2$  is heated, no reaction occurs.  *$PbO_2$*

88.2 and 87.7% pure.— $H_2S$  dild. with 15 times its vol. of air reacted with  $PbO_2$  at 0.125, 0.25, 0.5 and 1.0 atm. pressure. That the lower oxides of Pb render the  $PbO_2$  more active was confirmed by digesting impure  $PbO_2$  with dil.  $HNO_3$  to remove impurities and drying, after which treatment they behaved like pure  $PbO_2$ . Pure  $PbO_2$  did not react with  $SO_2$  but the impure samples reacted easily. That  $PbO_2$  treated with very dil.  $H_2S$  becomes inactive, indicates that the inactivity is caused by the formation of an adsorption compd. of  $PbO_2$  and  $H_2S$  before chem. action occurs. Impurities inhibit this adsorption compd. and accelerate the main reaction.

C. C. DAVIS

The period of induction in the precipitation of cuprous sulfide from sodium cuprous thiosulfate. G. SAMBAMURTY. *Proc. Sci. Assoc. Maharajah's College, Vizianagram*, Dec. 1922, 10-4.—A  $NaCuS_2O_3$  soln. (prepd. by treating  $CuSO_4$  soln. of d. 1.19 with  $Na_2S_2O_3$  soln. of d. 1.85 until colorless) acidified with an acid has a period of induction, the magnitude of which depends upon (1) the acid and (2) the concn. of the  $NaCuS_2O_3$ . The  $CuS$  first is colloidal and gives a blood-red soln., but later gives a reddish ppt. which turns successively brown, deep brown, greenish black and black. Concd.  $HCl$  has no secondary effect on the  $CuS$  and pptn. takes place normally. Concd.  $HNO_3$  greatly reduces the period of induction. With  $As_2O_3$  and with  $H_3PO_4$  a slight reddish color appears immediately but only after a long time does the color deepen. No pptn. occurs with  $(CO_2H)_2$  unless the soln. is warmed. Concd.  $H_2SO_4$  gives immediately black  $CuS$ . If uniformly increasing amts. of  $Na_2S_2O_3$  are added to a definite amt. of  $CuS_2O_3$  soln. and acid, the period of induction decreases, passes through a min., and again increases. The period of induction may be due to (1) a uo. of intermediate reactions or to (2) the inhibitive effect of colloidal S. Since  $HNO_3$  and  $HCl$  have approx. the same strength, the action of  $HNO_3$  in reducing the period is due not to successive reactions but to its oxidizing the colloidal S. Cause (2) is the more probable. With increasing concn. of  $Na_2S_2O_3$  the chances for coagulation of colloidal S are increased, the amt. in soln. is reduced and the pptn. of  $CuS$  occurs sooner. Above a certain  $Na_2S_2O_3$  concn., considerable acid is destroyed and the period increases again. Oxidizing agents, such as  $HClO_4$  and  $O_3$ , reduce the period of induction. This is not due to mech. agitation, since a rapid current of  $CO_2$  causes no decrease in the time of pptn. C. C. D.

The preparation of metallic phosphides from phosphine and metallic salt solutions. A. BRUKL. *Z. anorg. allgem. Chem.* 125, 252-6(1922).—Using the app. previously described for treating a Ag soln. with  $PH_3$  (cf. C. A. 16, 2822),  $Hg'$ ,  $Hg''$ , Pb and Cd solns. were treated with  $PH_3$ . Compds. were obtained which, unlike attempts previously reported in the literature, gave on analysis definite metallic phosphides. *Mercurous phosphide*,  $Hg_2P$ , prepd. from  $PH_3$  and  $Hg_2SO_4$  in dil.  $H_2SO_4$  was a black, flocculent, amorphous powder, rapidly oxidizing in the air with sepn. of metallic Hg. It is slowly oxidized by dil.  $HNO_3$  and liberates  $PH_3$  slowly when cold, rapidly when hot, with concd.  $HCl$ . Concd.  $H_2SO_4$  is reduced to  $H_2SO_3$ . *Mercuric phosphide*,  $Hg_2P_2$ , prepd. by mixing  $PH_3$  in alc. KOH with  $HgCl_2$  in  $Et_2O$ , was a brownish black ppt., turning gray in the air, not attacked by  $H_2O$ , alkalis or dil. acids in the cold, but decompd. by all of these when hot and oxidized by dil.  $HNO_3$ . It formed a double salt with  $HgCl_2$  which was successively dirty green, brown, orange and yellow and decompd. on heating. *Lead phosphide*,  $Pb_2P_2$ , prepd. by mixing  $Pb(OAc)_2$  in  $EtOH$  and  $PH_3$  in alc. KOH, was a black, flocculent ppt., decompd. slowly by cold  $H_2O$ , dil. acids and alkalis, rapidly when warm (cf. *Ann.* 231, 327(1885)). *Cadmium phosphide*,  $Cd_2P_2$ , prepd. from  $PH_3$  and dil. ammoniacal  $CdSO_4$ , was a black, flocculent ppt., decompd. by dil.  $HCl$ , oxidized by concd.  $HNO_3$  with a violent reaction, similar to  $Pb_2P_2$  towards other reagents.

C. C. DAVIS

Hollow pyramidal crystallization of alkali halides. HERMANN KUNZ-KRAUSE. *Ber. pharm. Ges.* 32, 329-34(1922).—An address, illustrative of the pyramidal crystn. of alkali halides, notably of  $NaCl$  and  $KI$ .

W. O. E.

**The alkali permanganates.** M. CRESPI AND E. MOLES. *Anales soc. españ. fis. quim.* 20, 555-62(1922).—All the alkali permanganates are similar in appearance.  $\text{LiMnO}_4$  was prepd. from  $\text{LiClO}_4$  and  $\text{KMnO}_4$ . It is readily sol. in  $\text{H}_2\text{O}$  and crystallizes with 2 mols.  $\text{H}_2\text{O}$ , in which it melts at  $180^\circ$  or a little below; decompn. begins at  $190^\circ$ ; d. 2.06.  $\text{NaMnO}_4$  was prepd. from  $\text{Na}_2\text{SO}_4$  and  $\text{Ca}(\text{MnO}_4)_2$  and also from  $\text{NaCl}$  and  $\text{AgMnO}_4$ . The soln. evapd. over  $\text{H}_2\text{SO}_4$  in vacuum yielded very deliquescent microscopic crystals contg. 1 mol.  $\text{H}_2\text{O}$ ; it decomposes at  $170^\circ$ ; d. 2.47.  $\text{NH}_4\text{MnO}_4$  was prepd. by treating  $\text{KMnO}_4$  with a great excess of  $\text{NH}_4\text{Cl}$ . Large crystals, d. 2.29, exploded on percussion or when heated to  $110^\circ$ . The aq. soln. can be evapd. at  $80^\circ$  without decompn.  $\text{RbMnO}_4$  and  $\text{CsMnO}_4$  were prepd. by adding the corresponding nitrates to a satd. soln. of  $\text{KMnO}_4$  at  $60^\circ$ . On cooling they crystd. out as anhyd.  $\text{RbMnO}_4$  d. 3.13, decomposes at  $259^\circ$ ; soly., 100 g. satd. soln. contains at  $2^\circ$ , 0.46 g.; at  $19^\circ$ , 1.06 g.; at  $60^\circ$ , 4.68 g.  $\text{CsMnO}_4$  d. 3.55, decomposes at  $320^\circ$ ; soly.  $1^\circ$ , 0.097 g.;  $19^\circ$ , 0.23 g.;  $60^\circ$ , 1.25 g. in 100 g. satd. soln. With the exception of the  $\text{NH}_4$  and  $\text{Na}$  salts the decompn. temps. are almost proportional to the mol. wts. ( $\text{KMnO}_4$  decomposes at  $240^\circ$ ). The thermal decompn. is similar throughout the series as was shown by detns. made of the amts. of  $\text{O}_2$  evolved by equimol. quantities. Cf. following abstract.

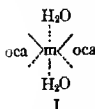
L. E. GILSON

**The alkaline earth permanganates.** M. CRESPI AND E. MOLES. *Anales soc. españ. fis. quim.* 20, 692-701(1922).—The permanganates of  $\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$  were prepd. and studied. The best method of prepn. is from equiv. quantities of the chloride and  $\text{AgMnO}_4$ . All are very deliquescent;  $\text{Ca}(\text{MnO}_4)_2$  cannot be obtained anhydrous even when heated to  $100^\circ$  in a vacuum desiccator. The existence of the various cryst. hydrates of  $\text{Ca}(\text{MnO}_4)_2$  and  $\text{Sr}(\text{MnO}_4)_2$  mentioned in the literature is denied. The densities of the  $\text{Ca}$ ,  $\text{Sr}$ , and  $\text{Ba}$  permanganates, as thoroughly dried as possible, are 2.49, 2.66, and 3.77, resp., and the decompn. temps.  $130^\circ$ ,  $175^\circ$ , and  $220^\circ$ . The quantity of  $\text{O}_2$  evolved from equimol. quantities when heated was detd. They all decompose in the same manner, and in a similar manner to the alkali permanganates (cf. preceding abstract). The equation of Askenasy and Solberg for the thermal decompn. of alkali permanganates,  $10\text{KMnO}_4 = 2\text{K}_2\text{MnO}_3 + (3\text{K}_2\text{MnO}_4 + 5\text{MnO}_2) + 6\text{O}_2$ , and the corresponding equation  $5\text{Ba}(\text{MnO}_4)_2 = 2\text{BaMnO}_3 + (3\text{BaMnO}_4 + 5\text{MnO}_2) + 6\text{O}_2$ , for alk. earth permanganates are considered correct.

L. E. GILSON

**Several optically active heavy metal complexes.** J. LIFSCHITZ. *Rec. trav. chim.* 41, 627-36(1922).—Heavy metal complexes with optically active coordinated groups have so far been obtained in but small nos. Volk (*C. A.* 7, 1193) obtained such derivs. of *l*-lactic acid. The spectroscopic and polariscopic study of the  $\text{Co}$  complexes of *l*- and *d*-propylenediamine (Werner, *C. A.* 12, 1861) raised a no. of questions (Lifschitz, Rosenbohm, *C. A.* 14, 1782; Lifschitz, *C. A.* 14, 3194). The color of many of these salts gives difficulty in the polariscope. Salt-forming derivs. of camphor form heavy metal complexes of high rotation and characteristic absorption. Hydroxymethylenecamphor (*A*),  $\text{C}_8\text{H}_{14}\text{CO.C:CHOH}$ , was best adapted for this purpose;  $\alpha$ -nitrocamphor (*B*),  $\text{C}_8\text{H}_{14}\text{CO.CHNO}_2$ , gives complexes to some extent which often show a surprising instability; isonitrosocamphor (*C*),  $\text{C}_8\text{H}_{14}\text{CO.C:NOH}$ , forms little characteristic complexes while camphorcarboxylic acid (*D*),  $\text{C}_8\text{H}_{14}\text{CO.CHCO}_2\text{H}$ , forms no metal complexes useful for this study. Further work is to be done with *C* and *D* and aminomethylene- and aminocamphor. The complexes obtained correspond to 2 formulas I and II in which *oca* represents *A*, and are brightly colored, well defined compds. which are little or not sol. in org. solvents. Only indications of the existence of isomers like

those obtained by W. and S. have been obtained. Contrary to Volk's observations these compounds showed no Cotton effect in the visible spectrum in spite of characteristic



absorption. The salts of trivalent metals showed very large rotations. The course of the rotation curve for the Co salt of *A* is quite analogous to that of K cobaltioxalate (Jaeger, *C. A.* 14, 1086), but it follows another type with Cr salts. Attempts to substitute *A* in Co derivs. thus (1)  $[(\text{NH}_3)_4\text{CoCO}_3]\text{Cl} + 2\text{A} \rightarrow [(\text{NH}_3)_4\text{Co oca}]_{\text{oca}}^{\text{Cl}} + \text{CO}_2 + \text{H}_2\text{O}$  and (2)  $[\text{en}_2\text{CoCO}_3]\text{Cl} + 2\text{A} \rightarrow [\text{en}_2\text{Co oca}]_{\text{oca}}^{\text{Cl}} + \text{CO}_2 + \text{H}_2\text{O}$  failed completely with (1) and were unsatisfactory with (2). Bishop, *et al.* (*Ann.* 281, 314 (1894)) obtained the  $\text{Fe}^{III}$  salt of *A* which shows such intense absorption that, in spite of its high rotation, good detns. could not be made. The acid copper salt varies in color from light green to dark green for the neutral salt in soln., depending on the degree of the dissociation expressed thus:  $\text{Cu oca}_2(\text{H oca})_2 \rightleftharpoons \text{Cu oca}_2 + 2\text{H oca}$ . This dissociation is favored in  $\text{CHCl}_3$  and  $\text{C}_6\text{H}_6$  but is small in  $\text{H}_2\text{O}$ . This Cu salt is a true inner complex salt: its EtOH soln. has an unusually low cond. The neutral Cu salt is obtained as a black-green mass from *A* in MeOH and  $\text{CuSO}_4 + \text{NaOAc}$  in  $\text{H}_2\text{O}$ . The presence of the acid salt is easily detected by its appearance under the microscope. The Ni salt was obtained similarly as light green crystals, sp. rotation  $\lambda 6680$  140°,  $\lambda 5940$  200°,  $\lambda 4700$  516° in  $\text{CHCl}_3$ . The  $\text{UO}_2$  salt was obtained similarly as an orange powder,  $\lambda 5940$  122° in  $\text{CHCl}_3$ . The prepn. of the cobaltous salt required care on account of its tendency to oxidize to the  $\text{Co}^{III}$  deriv. in air. It was obtained as a flesh-colored ppt.,  $\lambda 5940$  187° in  $\text{CHCl}_3$ . The Al salt was obtained similarly,  $\lambda 6250$  565°,  $\lambda 4490$  192.5° or for the latter a mol. rotation of about 10000°. Aq. solus. of Cr alum, KOAc and *A* in MeOH boiled under a condenser sep'd. the Cr salt of *A* as a peculiar grey-green salt. This salt, which has the simple mol. wt. in  $\text{C}_6\text{H}_6$ , shows a max. rotation at  $\lambda 5750$  of 580° and a min. at  $\lambda 5000$  to 5100 of -155°. The cobaltic salt is obtained by boiling aq. alc. *A* with  $\text{Co}(\text{OH})_2$  or even the hexammine salt. It shows a max. rotation at  $\lambda 6450$  860°, zero rotation at  $\lambda 6100$  and a min. at  $\lambda 5350$  with -3180°. On adding  $\text{FeCl}_3$  to aq. K campbornitronate (from *B*) and shaking the soln. out with  $\text{Et}_2\text{O}$  a soln. of the  $\text{Fe}^{III}$  salt of *B* is obtained. This salt decomposes in  $\text{Et}_2\text{O}$  in 5-10 mins. and could not be isolated. The Cr salt of *B* could not be obtained pure. A soln. of *B* + the calcd. amt. of KOH was treated with  $\text{CoCl}_2 + \text{NaOAc}$  soln. and extd. with  $\text{CHCl}_3$ . On evapg. the  $\text{CHCl}_3$ , the cobaltous salt of *B* was obtained as red needles; sp. rotation  $\lambda 5940$  250°.

E. J. WITZEMANN

DIELS, OTTO: Einführung in die anorganische Experimentalchemie. Berlin and Leipzig: W. de Gruyter Co. 446 pp.

FRIEND, J. NEWTON: Textbook of Inorganic Chemistry. Vol. 9. Pt. I. Cobalt, Nickel and the Elements of the Platinum Group. 2nd Ed. revised. London: Griffins. 392 pp. 18s.

SCHWARTZ, ROBERT: The Chemistry of the Inorganic Complex Compounds. An Introduction to Werner's Coordination Theory. Translated by Lawrence W. Bass. New York: John Wiley & Sons, Inc. \$1.75. 82 pp. Reviewed in *Am. J. Sci.* 5, 255 (1923).

## 7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL

Perchloric acid as a microchemical reagent. V. CORDIER. *Monatsh.* 43, 525-36 (1923).—In 1916 work was begun in the study of  $\text{HClO}_4$  as a microchem. reagent and

such work is now published although Denigès (*C. A.* 11, 2309, 2648) has in the meantime recommended  $\text{NaClO}_4$  for similar purposes.  $\text{HClO}_4$  like picric acid, and  $\text{H}_2\text{PtCl}_6$  forms characteristic salts not only with inorg. constituents like K and  $\text{NH}_4$  ions, but with a great many org. compds. particularly with basic compds., alkaloids, and carbonium, oxonium and thionium compds. In this paper, the use of a 40% soln. of  $\text{HClO}_4$  for detecting small quantities of the following substances is described: trimethylamine hydrochloride, tripropylamine, triisobutylamine, tetramethylammonium iodide, tetraethylammonium chloride, tetrapropylammonium iodide, phenylhydrazine, triphenylguanidine hydrochloride, hexamethylenetetramine, pyridine, quinoline, guinaldine, acridine, cinchonamine, scopolamine hydrobromide, cinchonine hydrobromide, cocaine, veratrine and guanine. Any one interested in the microchem. detection of these or similar compds. should consult the original article.

W. T. H.

Spectroscopic methods of analytical chemistry. C. AUER-WELSBACH. *Monatsh.* 43, 387-403(1923).—The methods are described in detail and will be published eventually in book form. In this, the first part of the treatise, the usefulness of spectroscopic work, the app. for spark spectra, optical testing, photographic testing and wave-length measurement are discussed.

W. T. H.

Iodometric estimations by Stortenbeker's method. D. DE MIRANDA AND A. E. ROEST VAN LIMBURG. *Chem. Weekblad* 18, 419-20(1921).—To det. the point at which Cl ceases to be evolved in iodometric estns. by Stortenbeker's method (*Z. anal. Chem.* 29, 273-80), a side branch with a tap is fused into the delivery tube of the retort, and connected by means of a ground-glass joint with a vessel contg. iodide-starch soln. The gas is periodically tested with this soln., and the latter eventually returned to the retort, thus avoiding loss.

Electroanalytical methods for the determination of metals from hydrochloric acid solution. A. J. ENGELBURG. *Z. anal. Chem.* 62, 237-84(1923).—Most electrolytic methods avoid the use of HCl solns. because of the danger of  $\text{Cl}_2$  being evolved at the anode which may attack the Pt anode or be diffused through the soln. by stirring and dissolve the cathode deposit. Schoch and Brown (*C. A.* 10, 2442), however, succeeded in using HCl solns. by adding such substances as  $\text{NH}_4\text{OH}$ , HCl, HCHO,  $\text{H}_2\text{C}_2\text{O}_4$ , or  $\text{H}_2\text{C}_4\text{H}_4\text{O}_4$  which undergo anodic oxidation more readily than does the Cl anion. The detns. of Sn, Cu, Sb, Bi, Pb and Cd have been studied anew with gauze electrodes of the type recommended by Fischer and with electrolytes stirred more rapidly. The procedures of S. and D. have been altered somewhat and some new methods have been devised. *Detn. of Sn.*—Expts. with the method of S. and B. gave results within 0.2% of the truth. Somewhat greater accuracy was obtained by the following procedure:—Dissolve Sn salt equiv. to about 0.3 g. Sn in 10 cc. concd. HCl, add 2 g.  $\text{NH}_4\text{OH}$ . HCl, dil. to 200 cc. and electrolyze at 35° with a current of 1.5 amp. With rapid stirring the deposition will be complete in 35 min. and results should be within 0.02% of the truth. *Detn. of Cu.*—S. and B. operated with a cathode potential of -0.40 volt against the normal calomel cell. Expts. now indicate that an e. m. f. of -0.75 volt against the  $\text{Hg}_2\text{Cl}_2$  electrode is most favorable for the deposition of Cu and this corresponds to the beginning of appreciable  $\text{H}_2$  evolution so that this may be used to designate the upper limit. With higher e. m. f. a quant. deposition of Cu is obtained but the deposits do not adhere well. To det. Cu, dissolve the Cu salt in 10 cc. of concd. HCl, add 2 g.  $\text{NH}_4\text{OH}$ . HCl and dil. to 200 cc. Electrolyze at 70°, keeping the cathode potential -0.75 volt to the  $\text{Hg}_2\text{Cl}_2$  cell. The deposition is complete in 7-20 mins. *Detn. of Sb.*—During the electrolysis the temp. should not be below 30° or explosive Sb will be formed. Above 70° there is too strong a tendency to hydrolyze and some danger of losing Sb by volatilization of the chloride. It is not necessary to use a coppered cathode. Dissolve Sb salt corresponding to not over 0.5 g. Sb in 10 cc. of concd.

HCl. Add 2 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$ , dil. to 200 cc. and electrolyze with the temp.  $50\text{--}70^\circ$  at the start, keeping the cathode potential  $-0.28\text{--}0.35$  volt to the  $\text{Hg}_2\text{Cl}_2$  cell. *Detn. of Bi.*—The method of S. and B. gives quant. deposition of the Bi but the deposits are so spongy that they are hard to handle. This may be obviated by adding a known quantity of Cu salt toward the end of the electrolysis so that the last of the Bi is deposited with Cu instead of with  $\text{H}_2$ . *Detn. of Pb.*—The method of S. and B. gives good results. Dissolve a weighed quantity of  $\text{PbCl}_2$  in 200 cc. of hot water contg. 10 cc. of concd. HCl. Add 2 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and electrolyze at  $60\text{--}70^\circ$  with a current of 1.5 amp. *Detn. of Cd and its sepn. from tin.*—Six expts. with the method of S. and B. showed that the method is good. *Sepn. of Sb and Sn.*—The modified procedure is as follows:—To a mixt. of  $\text{SnCl}_2$  and  $(\text{NH}_4)_2\text{SnCl}_6$  add 15 cc. of concd. HCl and 4 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$ . Dil. to 200 cc. and heat to  $60\text{--}70^\circ$ . Deposit the Sb first with the cathode potential  $-0.28\text{--}0.35$  v. to the  $\text{Hg}_2\text{Cl}_2$  cell. After the Sb detn., deposit the Sn at  $35^\circ$  with a current of 1.5 amp. The results of 13 expts. were remarkably accurate and indicate that the method is to be preferred to any other procedure for detg. Sn and Sb in the presence of one another. *The sepn. of Sb and Pb* can be accomplished similarly. *The simultaneous pptn. of Sb, Bi and Cu from electrolytes contg. HCl, Pb, Sn and Cd.*—The modified procedure is—To the soln. of the salts of these metals, add at least 20 cc. of concd. HCl and 4 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$ . Heat to  $55\text{--}75^\circ$  and electrolyze at a vol. of 200 cc. with a cathode potential of  $-0.20$  volt. If no deposition takes place, raise the potential to  $-0.35$  volt for a short while, decrease to  $-0.20$  volt until the current becomes weak and finish at  $-0.40$  volt as with Bi. *Sepn. of Sb from Bi and Cu.*—The method of S. and B. proved wrong in principle: the deposited metal always contained Sb and the electrolyzed soln. always contained some Cu. *The sepn. of Cd from Sn and Pb and of Bi from Sn* could not be accomplished by the method of S. and B. *The sepn. of Sn from Pb* is successful by the method of S. and B. *Detn. of Cd without the use of  $\text{NH}_4\text{OH} \cdot \text{HCl}$ .*—Dissolve the Cd salt in 10 cc. HCl, dil. to 200 cc. and electrolyze for 20 min. with a current of 1 amp. Add 20 g.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and 10–20 g.  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and continue to electrolyze for 40 min. with 1.2 amp. *Detn. of Zn.*—Dissolve 1 g.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  in 200 cc. of water contg. 1.5 cc. of HCl, add 2 g.  $\text{NH}_4\text{OH} \cdot \text{HCl}$  and electrolyze at  $18^\circ$  with a current of 4 amp. afterwards increased to 6–8 amps. About 15 mins. are required. *Sepn. of Cd from Zn.*—To 200 cc. of neutral soln. add 10 cc. of concd. HCl and electrolyze with 1 amp. for 40–60 min. to deposit Cd. Neutralize with NaOH, add 1.5 cc. concd. HCl and electrolyze at  $18^\circ$  with a current of 2 amp. eventually increased to 6–8 amp. *Sepn. of Sn from Zn and of Pb from Zn.*—The method of analysis is the same as with Cd and Zn except that 40 min. with 1.5 amp. is required for the quant. deposition of Sn. *Use of hydrazine sulfate in electrolysis.*—This salt may be used to replace  $\text{NH}_4\text{OH} \cdot \text{HCl}$  except in the detn. of Pb. *Use of  $(\text{NH}_4)_2(\text{SO}_4)_2$  in electrolysis.*—When evolution of  $\text{H}_2$  causes spangly deposits, this oxidizing agent will often serve to overcome this effect and it was found possible to work out a procedure where this substance alone was added to a HCl soln. (detn. of Cu) or where it was used in conjunction with  $\text{NH}_4\text{OH} \cdot \text{HCl}$  (detn. of Sn and Sb). Also by observing the cathode potentials it is possible to get fair qual. tests for Bi, Cu, Sb, Sn, Cd and Pb.

W. T. HALL

▲ A new method of microsublimation. R. KEMPF. *Z. anal. Chem.* 62, 284–93 (1923).—An app. is described which consists of an elec. hot plate mounted on a porcelain base and connected with resistances so that the temp. can be kept const. within  $1^\circ$ . By placing the substance in a thin layer upon the heating plate and keeping an object glass about 0.1–0.01 mm. above it, substances can be sublimed which have hitherto required sublimation in a vacuum to prevent decompn. It is also possible to work with the app. in a vacuum. Photomicrographs made with the app. are shown of  $\text{S}_2$ , benzoic

*acid indigo, alizarin, theine, theobromine, vanilla, Sapanine and human blood.* Under atm. pressure the following are the minimum temps. at which sublimates can be obtained with a few common substances:  $\text{HgCl}_2$ , 17°; S, 50°; As, 50°; benzoic acid, 19°; *o*-nitrobenzoic acid, 35°; *o,p*-dinitrobenzoic acid, 61°; stearic acid, 38°; caffeine, 25°; theobromine, 91°; vanillin, 53°; alizarin, 45°; indigo, 95°; cocaine, 36°; morphine, 100°; strychnine, 103°. The app. can be obtained from Heraeus. W. T. HALL

Sliding scales for the convenient titration of strong liquids by dilution and use of aliquot parts. C. H. D. CLARK. *Analyst* 48, 61-3 (1923).—A very simple slide rule is described which can be made easily out of a piece of folded foolscap. The rule has proved useful for comparing the concns. of many solns. of varying strengths with that of a single standard. W. T. H.

The application of conductivity titrations in precipitation analysis. VIII. Conductivity titrations with lithium oxalate. I. M. KOLTHOFF. *Z. anal. Chem.* 62, 161-78 (1923).—Ag, Pb and Cu ions can be titrated by the conductometric method with  $\text{Li}_2\text{C}_2\text{O}_4$  as reagent. With Cd and Zn the results are unsatisfactory. Titrations of Ni, Co, Fe and Mn ions are not accurate and the formation of complexes is indicated. Ba and Sr can be titrated accurately but Mg cannot because of complex formations. Strong acids, *i. e.*, H ions, can be titrated and inflections on the cond. curve correspond to the formation of tetroxalate and binoxalate but not to the formation of free oxalic acid. Ca solns. even when quite dil. can be titrated, but in the latter case the addition of alc. is desirable. Mg influences the titration of Ca. In very dil. solns. the sum of the Ca and Mg is indicated and consequently the hardness of water can be shown by titration with  $\text{Li}_2\text{C}_2\text{O}_4$ . The metals of the Cu and Fe groups also interfere with the titration of Ca even in ammoniacal soln. IX. Conductivity titrations with potassium ferrocyanide. *Ibid* 62, 209-14.—Owing to the formation of double salts, conductometric titrations with  $\text{K}_2\text{Fe}(\text{CN})_6$  are not very successful. Pb alone can be titrated with accuracy. In very weak ammoniacal solns. it is also possible to titrate Zn. X. Conductivity titrations with potassium ferricyanide. *Ibid* 214-5.—A no. of successful titrations were made with Ag, Cu, Cd, Co and Ni but the end points are not very sharp. XI. Conductivity titrations with sodium nitroprusside. *Ibid* 216-7.—Ag was the only metal which could be titrated in spite of the fact that many other insol. compds. can be obtained. W. T. HALL

The electrometric titration of molybdenum with a titanous salt. H. H. WILLARD AND FLORENCE FENWICK. *J. Am. Chem. Soc.* 45, 928-33 (1923).—Previous attempts by ordinary titration to det. Mo by reducing it from the 6-valent to 5-valent condition with 3-valent Ti have failed because of difficulty in getting a suitable indicator to show the end point. By electrometric titration, with a bimetallic electrode, it was found possible to det. the end point within 0.4 cc. of 0.05 *N* Ti soln. The method may be applied to the detn. of Mo in alkali molybdates and to the detn. of P as well as Mo in steel. The presence of V appears to help rather than hinder the reaction. W. T. H.

The electrometric titration of selenium in the presence of tellurium, iron and copper. H. H. WILLARD AND FLORENCE FENWICK. *J. Am. Chem. Soc.* 45, 933-9 (1923).—Although the character of the end point is somewhat different from that in most electrometric titrations, it is possible to titrate with a bimetallic electrode and  $\text{TiCl}_3$  soln. and get 4-valent Se reduced to metal in cold, HCl soln. satd. with NaCl. The results are accurate to within 0.1 mg. Se. Under these conditions, Te is not reduced and its only effect is to modify the end point. The titration is not affected by moderate quantities of  $\text{H}_2\text{SO}_4$  and although bivalent Fe is formed the proper values for Se are obtained. The reducing effect of trivalent Ti upon mixts. of bivalent Cu and quadrivalent Se is selective and first Se and then Cu may be detd. by a single titration. W. T. HALL

An electrometric study of the neutralization of phosphoric acid by calcium hydroxide. G. H. WENDT AND A. H. CLARKE. *J. Am. Chem. Soc.* **45**, 881-7(1923).—In the titration of  $\text{H}_3\text{PO}_4$  with  $\text{Ca}(\text{OH})_2$ , the usual titration curve is obtained up to the formation of  $\text{CaH}_2(\text{PO}_4)_2$ , but a ppt. of  $\text{Ca}_3\text{H}_4(\text{PO}_4)_2$  appears soon afterward. This appears as a transitory phase and the only electrometric end points are at  $p_H = 4$  corresponding to the formation of  $\text{CaH}_2(\text{PO}_4)_2$  and at  $p_H = 8.5$  corresponding to the complete formation of  $\text{Ca}_3(\text{PO}_4)_2$ . Under equil. conditions only these 2 salts are formed.

W. T. HALL

The volumetric determination of trivalent iron and of copper in the presence of iron. F. L. HAHN AND H. WINDISCH. *Ber.* **56B**, 598-601(1923).—Mohr's iodometric detn. of  $\text{Fe}^{+++}$  requires a considerable excess of KI and even then the reduction of the  $\text{Fe}^{+++}$  is not as rapid as is desirable. If a little  $\text{Cu}_2\text{I}_2$  is present, however, and this may be easily made by adding KI to  $\text{Cu}^{++}$  soln. and removing the liberated  $\text{I}_2$  with  $\text{Na}_2\text{S}_2\text{O}_3$  soln., the reaction between  $\text{Fe}^{+++}$  and KI is accelerated greatly and only  $1/20$  as much KI is required. Thus 20 cc. of 0.1 *N*  $\text{FeCl}_3$  soln. treated with 0.35 g. KI and 0.2 mg.  $\text{Cu}_2\text{I}_2$  are reduced quantitatively when the liberated  $\text{I}_2$  is titrated with  $\text{Na}_2\text{S}_2\text{O}_3$ . A large excess of  $\text{Cu}_2\text{I}_2$  does no harm. Because of the large equiv. wt. of Fe alum (482) as compared with  $\text{K}_2\text{Cr}_2\text{O}_7$  (49) the advantage of the former salt as an iodometric standard is apparent. It is well known that the presence of Fe interferes with the iodometric detn. of Cu but the effect may be prevented by adding 2 mols. of  $\text{PO}_4$  for each mol. of Fe present. If the soln. is strongly acid, this may be accomplished by adding  $\text{Na}_2\text{HPO}_4$  soln. If the soln. is nearly neutral it is better to take the requisite vol. of  $\text{Na}_2\text{HPO}_4$ , add *p*-nitrophenol and then  $\text{H}_3\text{PO}_4$  until the soln. is decolorized and add this  $\text{NaH}_2\text{PO}_4$  soln. to the  $\text{Cu}^{++}$  soln. In the absence of the  $\text{PO}_4$ , the iodometric titration gives the sum of the  $\text{Fe}^{+++}$  and  $\text{Cu}^{++}$  present.

W. T. HALL

The determination and separation of arsenic, antimony and tin. K. K. JÄRVINEN. *Z. anal. Chem.* **62**, 184-204(1923).—For analysis a sample contg. about 0.3 g. of these elements is suitable. For the distn. of  $\text{AsCl}_3$  it is necessary that the As should all be in the trivalent condition and only HCl or  $\text{H}_2\text{SO}_4$  be used. If  $\text{HNO}_3$ , HI, org. substances, or metal sulfides are present, place the sample for analysis in a 300 cc. Kjeldahl flask and add concd.  $\text{HNO}_3$  equiv. to the halogen acid and about 15 cc. of concd.  $\text{H}_2\text{SO}_4$ . Place a little pumice in the flask and heat over a flame until  $\text{H}_2\text{SO}_4$  boils and has rinsed the mouth of the flask. Allow the  $\text{H}_2\text{SO}_4$  soln. to cool and add 1 g.  $\text{Na}_2\text{S}_2\text{O}_3$  crystals. Boil until almost all of the S has been expelled and all sulfide has been decomposed. Cool, and rinse into a 400 cc. flat-bottomed flask, using first 80 cc. of water and finally 60 cc. of concd. HCl. If the latter does not dissolve all of the As, Sb and Sn compds. in the original flask, add a little hot NaOH soln. and transfer to the other flask. To the soln. add 25 cc. of 20% KBr soln. and 1 g.  $\text{Na}_2\text{SO}_3$ . Next distill off the  $\text{AsCl}_3$ . To prevent loss of some Sb, the use of a 50 cm. long Young's dephlagmator is advised. Provide this dephlagmator with a thermometer and condenser. As receiver use a 500 cc. flat-bottomed flask contg. 200 cc. of water. When, after boiling the soln., the residual soln. is reduced to 60 cc., stop distg. After a few min. add 50 cc. of 6 *N* HCl and a little more sulfite. Distill again until only about 60 cc. of soln. remain. Finally add 40 cc. of water and distill over about 20 cc. to rinse out the app. Boil the distillate (10-15 min.) till all of the  $\text{SO}_2$  and not more than 50 cc. of water have been expelled and titrate the trivalent As at about 80° with 0.05 *N*  $\text{KBrO}_3$ , methyl orange being used as indicator. Run a blank with the reagents. Some samples of methyl orange have proved unsuitable for the titration. Transfer the distn. residue back to the Kjeldahl flask, add 20 cc. of concd.  $\text{HNO}_3$  and a little  $\text{H}_2\text{SO}_4$  if necessary to bring its vol. up to 15 cc. Evap. and reduce with  $\text{Na}_2\text{S}_2\text{O}_3$  as before. Cool, add 60 cc. of water and 5-10 cc. of concd. HCl and boil gently for a few mins. to remove  $\text{SO}_2$ . Titrate the Sb with 0.05 *N*  $\text{KBrO}_3$  soln. For the Sn detn.



rinse the soln. into an Erlenmeyer flask, add 0.5 g. of Fe powder, close the flask with a Bunsen valve and heat on the water bath about 1 hr. To the soln. at about 70° add about 0.5 g. more of Fe powder and a little more after 10 min. Filter through a paper filter into a 500 cc. Kjeldahl flask. To remove traces of Sn from the pptd. Sb, rinse the ppt. back into the Erlenmeyer flask, dissolve it by boiling with 20 cc. concd. HCl and finally adding a little  $\text{KClO}_3$  or  $\text{Br}_2$  water. Treat again with Fe as before and filter. Conc. the  $\text{SnCl}_2$  soln. to about 50 cc., transfer it, with not over 50 cc. of 6 *N* HCl, into a 200 cc. flat-bottomed flask, stopper the flask with a meter-long tube constricted at the top and connected by a long piece of rubber tubing with a 150 cc. pipet that dips into a cylinder contg. a little water. For each 100 cc. of Sn soln. add at least 6 g. of Fe powder and reduce on the water bath till all Fe is dissolved (30 mins.). Cool and titrate promptly with  $\text{I}_2$  soln. The entire analysis requires about 6 hrs. W. T. H.

**Separation of arsenic, antimony and tin.** F. L. HAHN. *Z. anorg. allgem. Chem.* 123, 276(1922).—The sepn. of Sb by oxidation to pyroantimonate (cf. Hampe, *Chem. Ztg.* (18, 1900–1(1894)) can be employed for the estn. of Sb in the presence of As and Sn. J. S. C. I.

**The separation of arsenic from other elements.** N. TARUGI. *Gazz. chim. ital.* 52, II, 323–32(1922).—The different temps. of volatility of the chlorides of As, Sb and Sn were first used by Emil Fischer (*Ber.* 13, 1778(1880)) for the sepn. of these elements. The various methods since developed for utilizing this principle of differing volatility are reviewed and found to involve inconvenience either through the use of gaseous reagents or extraneous substances. T. first tried to use HCOH as a substitute for reducing agents previously recommended but got negative results. An observation of Jannasch and Seidel (*C. A.* 4, 2245) on the behavior of  $\text{N}_2\text{H}_4 + \text{KBr}$  on  $\text{H}_3\text{AsO}_4$  was then utilized. 10 cc. 0.1 *N*  $\text{Na}_2\text{HAsO}_4 + 10$  cc. 30%  $\text{NaOH} + 2.3$  g.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  were heated 0.5 hr. in a distg. flask. 100 cc. concd. HCl were then added and the mixt. was distd. for 1.5 hrs. The distillate gave  $\text{As}_2\text{O}_3$  with  $\text{H}_2\text{S}$  equiv. to 0.0745 g. As (calcd. 0.075 g.). A similar distillate titrated with 0.1 *N* I–KI gave 0.0744 g. As (calcd. 0.075 g.).  $\text{Sb}_2\text{O}_3$  treated similarly and distd. showed no Sb in the distillate. The sepn. of As and Sb was sharp and accurate. Similar tests on the distn. of Pb, Hg and Fe showed that these elements are not volatile under these conditions, while the sepn. of each of them in succession from As gave accurate results. The method has the advantage of avoiding the use of reagents likely to be contaminated with As such as  $\text{SO}_2$  or sulfites and permits of direct titration of the  $\text{As}_2\text{O}_3$  in the distillate. B. J. WITZEMANN

**Experiments relative to the determination of uranium by means of cupferron.** JAMES A. HOLLADAY and THOMAS R. CUNNINGHAM. *Trans. Am. Electrochem. Soc.* 43, preprint.—U in the quadrivalent or lower form may be quant. pptd. with cupferron from solns. contg. 4–8%  $\text{H}_2\text{SO}_4$ . Al, Ca, Mg, Zn, and P remain in soln. The ppt.  $\text{U}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$  may be quant. converted by ignition to  $\text{U}_3\text{O}_8$ . V is pptd. with U and is sepd. by dropping the cupferron ppt. into an Erlenmeyer flask, treating with  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  and evapg. to dryness. Successive portions of  $\text{HNO}_3$  destroy the carbonaceous matter, the acid is then expelled, and V detd. by titration with  $\text{KMnO}_4$ . Exptl. results show the limits of acidity for complete pptn., the completeness of conversion of  $\text{U}(\text{C}_6\text{H}_5\text{N}_2\text{O}_2)_4$  to  $\text{U}_3\text{O}_8$  by ignition, and the sepn. of U from Al, Ca, Mg, and P by regulation of the acidity. U and V may be sepd. and detd. in the presence of Al, Ca, Mg, Fe, and P by having the U, V, and Fe in the hexa-, penta-, and tervalent forms, resp. Pptn. is effected with cupferron in a 12%  $\text{H}_2\text{SO}_4$  soln. The cupferron is destroyed by  $\text{HNO}_3$  and the U reduced by passage through a Jones reductor. U is again pptd. in 6%  $\text{H}_2\text{SO}_4$  soln. and ignited to  $\text{U}_3\text{O}_8$ . W. H. BOYNTON

**The quantitative determination and separation of barium and strontium.** R. LEO. *Monatshefte* 43, 567–88(1923).—The fluosilicate method for pptg. Ba and sepg. it from

Sr was studied and as a result a method devised which appears to be as satisfactory as the chromate method. The soly. of  $\text{BaSiF}_6$  is diminished by using  $(\text{NH}_4)_2\text{SiF}_6$  instead of  $\text{H}_2\text{SiF}_6$  as reagent. The ppt. when dried at  $180^\circ$  gives results which are somewhat too high, owing to the presence of a small quantity of water. By heating to a higher temp. in an electric oven only a partial conversion to  $\text{BaF}_2$  was effected. When pptd. in the presence of Sr, some of this element is pptd. with  $\text{BaSiF}_6$  although the soly. of  $\text{SrSiF}_6$  is very much greater than would permit pptn. if Sr alone were present. By warming the ppt. for 10 min. with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  the  $\text{BaSiF}_6$  and  $\text{SrSiF}_6$  is converted into  $\text{BaCO}_3$  and  $\text{SrCO}_3$  which are easily dissolved by dil. acid so that the pptn. of the Ba can be repeated and a quant. sepn. made. It is well to proceed as follows:—To 50 cc. of soln. contg. 0.3–0.5 g. of Ba and Sr, add 6–10 cc. of  $N$  HCl per 100 cc. of soln. and treat at room temp. with a slight excess of 10%  $(\text{NH}_4)_2\text{SiF}_6$  soln. Compute the vol. of the reagent on the assumption that the sum of the Ba and Sr is all Ba and add 10–50% in excess of the theoretical quantity. After most of the Ba has been pptd., wait 30 mins. and then add  $1/3$  of the soln.'s vol. of alc. After 2–3 hrs. filter and wash the ppt. 2–3 times with 50% alc. satd. with  $(\text{NH}_4)_2\text{SiF}_6$ . Rinse the ppt. into a dish and heat on the water bath with an excess of  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$ , stirring frequently. When the  $\text{BaCO}_3$  has assumed a coarsely granular character, filter, wash with dil.  $\text{NH}_4\text{OH}$  and finally dissolve in a little hot, dil. HCl. Dil. and repeat the pptn. of  $\text{BaSiF}_6$  under the same conditions as before. After igniting the filter and the ppt. transform it into  $\text{BaSO}_4$  by heating with  $\text{H}_2\text{SO}_4$  and HF. To det. Sr in the filtrate from the  $\text{BaSiF}_6$  either ppt.  $\text{SrSO}_4$  by a little  $\text{H}_2\text{SO}_4$  and alc. or evap. to dryness with  $\text{H}_2\text{SO}_4$ , heat to expel  $(\text{NH}_4)_2\text{SO}_4$ , etc., and weigh the residual  $\text{SrSO}_4$ . The detn. of Ba in the presence of Sr was also studied with the use of  $\text{Na}_2\text{S}_2\text{O}_3$  as precipitant. If the pptn. is carried out twice the results are very satisfactory when considerable Ba is present with little Sr, but when considerable Sr is present it contaminates even the second ppt. Soly. data on  $\text{BaSiF}_6$ ,  $\text{SrSiF}_6$ ,  $\text{Ba}_2\text{S}_2\text{O}_3$  and  $\text{Sr}_2\text{S}_2\text{O}_3$  are given.

W. T. H.

**Estimation of the alkali metals as sulfates.** N. SCHOORL AND I. M. KOLTHOFF. *Chem. Weekblad* 17, 425–7 (1920).—Van Duin's conclusions (*C. A.* 14, 2454) that in the conversion of pyrosulfate to normal sulfate by ignition with  $(\text{NH}_4)_2\text{CO}_3$ , errors are introduced, (a) by the presence of unburned C (especially in the case of alkali salts of org. acids), and (b) by the loss of alkali sulfate with the volatile  $\text{NH}_4$  salts in the ignition, are investigated, and shown to be untrue. All residual C is destroyed by repeated heating with strong  $\text{H}_2\text{SO}_4$  in a closed crucible, care being taken not to evap. off the acid too quickly. If, after this, the colorless pyrosulfate residue be further strongly heated, it solidifies on the walls of the crucible, disengaging  $\text{SO}_2$ . If a fragment of  $(\text{NH}_4)_2\text{CO}_3$  is added while the crucible is kept at this temp., it does not volatilize violently, but assumes a condition analogous to the spheroidal state, and disappears slowly and quietly. This procedure gives accurate results. The method suggested by van Duin, evap. the pyrosulfate with  $(\text{NH}_4)_2\text{CO}_3$  soln. and igniting the residue, is open to many objections; thus, alkali carbonates are formed in the soln., and the tendency to spatter is not diminished, but increased, because the crystals formed as the soln. is evapd. enclose another liquor.

J. C. S.

**The titration of mercuric ions with chloride ions and the application of this titration to the analysis of cinnabar and of organic mercury compounds.** E. VOROČEK AND L. KAŠPÁREK. *Bull. soc. chim.* 33, 110–22 (1923).—When Cl ions are added to a soln. contg. Hg (ic) ions (from the sulfate or nitrate) 99.07% of the latter are converted into nonionized  $\text{HgCl}_2$  by the addition of an equiv. amt. of NaCl. The end point of the reaction can be detected by forming a slight ppt. of  $\text{HgFeNO}(\text{CN})_6$ , which will not dissolve upon addition of NaCl soln. until the rest of the Hg has reacted. The ppt. dissolves best in a hot soln. but the titration is best made at room temp. because the

transformation into  $\text{HgCl}_2$  is more nearly quant. at lower temps. To det. Hg in a ppt. of  $\text{HgS}$ , treat each 0.25 g. of ppt. with 50 cc. of a mixt. of concd.  $\text{HNO}_3$  with twice its vol. of concd.  $\text{H}_2\text{SO}_4$ . Heat in a Kjeldahl flask until the liquid is clear and for 10 mins. longer. It is not necessary for all the Hg to be in soln. but all of the S must be oxidized. Cool, dil. with water and remove all  $\text{HNO}_3$  by treatment with  $\text{KMnO}_4$ . Dil. to 1 l. and take an aliquot of 100-200 cc. for the analysis. For the titration, add 0.06 g. of Na nitroprusside and titrate in a vol. of about 200 cc. with 0.1 N NaCl until the soln. is clear. Calc. the result on the assumption that 0.9907 atom of Hg reacts with  $\frac{1}{2}$  atom of Cl. The results are then accurate to 0.2%. Native cinnabar can be analyzed in the same way, but the original digestion of 0.3 g.  $\text{HgS}$  requires about 6 hrs. In the analysis of org. compds. the same method of decompn. can be used but it is better to use  $\text{HNO}_3$  and  $\text{KMnO}_4$ . Use 15-20 cc. of concd.  $\text{HNO}_3$  for each g. of substance, heat on the water bath and add powdered  $\text{KMnO}_4$  in small portions until the color of the latter is retained for 3 mins. About 6 g. of this reagent are usually required for 1 g. of substance. After the decompn., cool and dissolve any ppt. of  $\text{MnO}_2$  by the careful addition of  $\text{NaNO}_2$  soln. Then add  $\text{H}_2\text{SO}_4$ , remove the excess nitrite with a satd. soln. of  $\text{KMnO}_4$ , dil. and titrate. To analyze an org. compd. contg. halogen it is necessary to get the Hg away from the halogen. This may be accomplished by decomposing the substance with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , dilg. and pptg.  $\text{HgS}$ . The ppt. can be analyzed as already described. The presence of Pb, Zn, Al, Fe, Cr and Ca in soln. does not influence the accuracy of the titration.

W. T. HALL

Determination of zinc in minerals. E. OLIVIER. *Mon. sci.* 13, 31-5(1923).—The  $\text{Na}_2\text{S}$  titration until a drop of the soln. turns  $\text{PbCO}_3$  paper black is preferred in French labs. for the technical assay of Zn ores. The method is described in detail, starting with the dissolving of the ore.

W. T. H.

The estimation of nickel in steels. C. N. WATERHOUSE. *Chem. Trade J.* 72, 327(1923).—Dissolve 1 g. of steel in 20 cc. of 6 N HCl. Oxidize with a little  $\text{HNO}_3$  and boil off nitrous fumes and excess acid. Add 20 cc. of satd. citric acid soln. and sufficient 6 N  $\text{NH}_4\text{OH}$  nearly to neutralize the acid. Cool, neutralize carefully to litmus and 5 cc. in excess. Add 6 cc. of freshly prepared, 5% KI soln. and titrate with KCN and  $\text{AgNO}_3$  in the usual way.

W. T. HALL

Determination of magnesium in the aluminium alloys. BUNTARO OHTANI. *J. Chem. Ind. (Japan)* 25, 1305-10(1922).—The ordinary method of detn. of Mg in Al alloys makes removal of Al from the final ppt. very difficult. An addn. of tartaric acid eliminates this difficulty because Al forms sol. complex salt with tartaric acid. The initial addition of tartaric acid should be 1.5 times that of Al. Com. tartaric acid is likely to contain enough Ca to cause the pptn. of Ca phosphate; a blank Mg detn. with all the reagent should be run.

S. T.

Estimation of iron and aluminium in natural phosphates. O. NYDEGGER AND A. SCHAUS. *Bull. fed. ind. chim. Belg.* 1, 405-7(1922).—Von Gruber's method (Prost. Manuel d'anal. Chim., 105) consists in neutralizing the soln. of the phosphate in HCl with 20% NaOH, adding an excess of the latter, boiling the soln. to convert  $\text{AlPO}_4$  into  $\text{NaAlO}_2$ , filtering, acidifying the soln., and pptg. the Al as phosphate by means of  $\text{NH}_3$ . The Fe is estd. by titration with  $\text{KMnO}_4$ . This method is, however, inaccurate, as the Al is not pptd. quantitatively as phosphate; the preliminary prepn. of the soln. removes  $\text{H}_3\text{PO}_4$ , so that insufficient remains. The error is obviated by the following procedure: Dissolve 12.5 g. of the phosphate in HCl and evap. the soln. to dryness to render the silica insol. Again dissolve in HCl, dil. the soln., boil and make up to 250 cc. Of this, use 100 cc. for estn. of Fe and a further 100 cc. for Al. To the latter add 10-20 cc. of a 10% soln. of  $\text{Na}_2\text{HPO}_4$ , neutralize the whole with NaOH, add a further 20 cc. of  $\text{Na}_2\text{HPO}_4$  soln. and boil the mixt. for 5 mins., or until the ppt. is of a brick-red

color. After cooling, dil. the soln. to 250 cc., filter, acidify 100 cc. of the filtrate (equiv. to 2 g. of phosphate) with HCl and ppt. the Al as phosphate with  $\text{NH}_3$ , taking care to avoid an excess of the latter. Control expts. show this modification of the method to be trustworthy.

J. S. C. I.

**The qualitative detection of chlorine, bromine, iodine and silver in the corresponding silver halides.** H. SCHMALFUSS. *Z. anal. Chem.* 62, 220-31(1923).—To a mixt. of pure Ag halides add  $(\text{NH}_4)_2\text{CO}_3$  soln. to ext. AgCl and test the ext. with KBr; a ppt. of AgBr indicates the presence of AgCl. Treat the residual salt from the  $(\text{NH}_4)_2\text{CO}_3$  treatment with  $\text{H}_2\text{S}$  soln. and filter off the ppt. of  $\text{Ag}_2\text{S}$ . To one half of the filtrate add  $\text{HNO}_2$  to liberate  $\text{I}_2$  from HI and test by shaking with  $\text{CS}_2$  for  $\text{I}_2$ . To the other half of the filtrate add  $\text{Cl}_2$  sufficient to oxidize I to  $\text{HIO}_3$  and test for  $\text{Br}_2$  with  $\text{CS}_2$ . If considerable iodide is present it is better to decant off the soln. from the iodide test and apply the test with  $\text{Cl}_2$  to this soln.

W. T. H.

**A general method for the detection of easily volatile acids.** G. KAROLANOV. *Z. anal. Chem.* 62, 217-22(1923).—In qual. anal. a sep. group may be made of acids which are easily volatile or whose salts are easily decomposed— $\text{H}_2\text{S}$ , HCN,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{S}_2\text{O}_3$ ,  $\text{HNO}_3$  and  $\text{HClO}_4$ . Of these acids, all but  $\text{H}_2\text{S}_2\text{O}_3$  give products volatile enough to serve for their identification when an indifferent gas (e. g.,  $\text{H}_2$ ) is passed through a soln. in 2 N AcOH at room temp. To test for these acids use  $\text{AgNO}_3$  soln. for HCN,  $\text{Ph}(\text{OAc})_2$  soln. for  $\text{H}_2\text{S}$ , diphenylamine soln. for  $\text{HNO}_3$ , dil. starch-iodide soln. for  $\text{H}_2\text{SO}_3$ , indigo soln. for  $\text{HClO}_4$  and  $\text{Ba}(\text{OH})_2$  for  $\text{H}_2\text{CO}_3$ . If considerable  $\text{H}_2\text{S}_2\text{O}_3$  salt is present it will be decomposed by the AcOH, otherwise it may be necessary to add a little concd.  $\text{H}_2\text{SO}_4$ . The following procedures are based upon this behavior: *Detection of sulfite in the presence of thiosulfate.*—Dil. the soln. until AcOH causes no deposition of S. Add to 2 N AcOH in a small flask and introduce a stream of  $\text{H}_2$ . If  $\text{H}_2\text{SO}_3$  is present the vapors will decolorize starch-iodide soln. To detect  $\text{H}_2\text{S}_2\text{O}_3$  add a little concd.  $\text{H}_2\text{SO}_4$  to the AcOH soln.; a ppt. of S will form if a salt of  $\text{H}_2\text{S}_2\text{O}_3$  is present. *Removal and test for sulfide in the presence of sulfite and thiosulfate.*—To the neutral soln. contg. the salts of these 3 acids, add  $\text{ZnCl}_2$  soln. and filter. Test the filtrate as above. Place the Zn ppt. in another portion of AcOH and pass the  $\text{H}_2$  gas from the flask into  $\text{Pb}(\text{OAc})_2$  soln. *Test for nitrite in the presence of nitrate, chlorate, etc.*—Place the substance in the 2 N AcOH, introduce  $\text{H}_2$  and pass the gas from the flask over a drop of diphenylamine soln. A blue cloud will form if  $\text{HNO}_2$  is present and the more stable acids named do not affect the test. *Detection of hypochlorous acid in the presence of chloric and perchloric acids.*—When passed through 2 N AcOH contg. a hypochlorite,  $\text{H}_2$  gas carries over enough  $\text{HClO}$  to decolorize a very dil. soln. of indigo.  $\text{HClO}_3$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ , etc., do not interfere with the test. *Detection of cyanide in the presence of chloride, bromide, ferrocyanide, ferricyanide, etc.*—Simple cyanides are decomposed by 2 N AcOH sufficiently to give the typical pptn. with  $\text{AgNO}_3$  soln. or the Prussian blue test when the vapors are tested. Salts of the other acids mentioned remain unaffected. *Detection of carbonate and hypochlorite.*—These two acids do not interfere with one another and they may be detected by testing the vapors with  $\text{Ba}(\text{OH})_2$  and indigo solns. separately. *Detection of carbonate and sulfide.*—These acids also cause no interference and sep. tests of the vapors may be made with  $\text{Ba}(\text{OH})_2$  and  $\text{Ph}(\text{OAc})_2$  solns. *Detection of cyanide and sulfite.*—Pass the gas from the flask first into a soln. of  $\text{AgNO}_3$  in dil.  $\text{HNO}_3$  to detect HCN and from thence into starch-iodide soln. to detect  $\text{H}_2\text{SO}_3$ . *Detection of cyanide and sulfide.*—Pass the vapors first into an AcOH soln. of  $\text{Ph}(\text{OAc})_2$  to detect  $\text{H}_2\text{S}$  and then into an  $\text{HNO}_3$  soln. of  $\text{AgNO}_3$  to detect HCN. *Detection of sulfite, cyanide and carbonate.*—In this test four tubes are necessary, one after the other. The first should contain  $\text{AgNO}_3$  to detect the HCN, the second very dil. iodide of starch to detect  $\text{H}_2\text{SO}_3$ , then concd.  $\text{KI}_3$  soln. to remove all  $\text{H}_2\text{SO}_3$  and finally  $\text{Ba}(\text{OH})_2$  to detect  $\text{H}_2\text{CO}_3$ .

*Detection of cyanide, sulfide, sulfite, thiosulfate and carbonate.*—Treat the neutral soln. with  $\text{ZnCl}_2$  soln. Test the ppt. for  $\text{H}_2\text{CO}_3$ ,  $\text{HCN}$  and  $\text{H}_2\text{S}$  as already described and the soln. for  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}_2\text{O}_8$ .

W. T. HALL

*Sensitive reaction for copper, thiocyanates, and pyridine.* G. SPACU. *Bul. soc. Stiinta Cluj* 1, 284-91(1922).—A compd. insol. in water and having the formula  $\text{CuPy}_2(\text{CNS})_2$  ( $\text{Py}$  = pyridine) is formed on adding a neutral soln. of a thiocyanate and a few drops of pyridine to a neutral soln. of a Cu salt. The pyridine should be added before the thiocyanate soln., as otherwise a dark ppt. of Cu thiocyanate is thrown down in concd. solns. In employing the reaction to detect Cu, strongly acid solns. must be evapd. and feebly acid solns. neutralized by the addn. of pyridine, care being taken to avoid the addn. of excess, as the ppt. is sol. in pyridine. The reaction is sensitive to 1:300,000 as a test for Cu, to 1:2000 for pyridine, and 1:50,000 for thiocyanates. The sensitiveness can be increased to 1:800,000 for Cu by shaking the mixed solns. with several drops of  $\text{CHCl}_3$ , which assumes an emerald-green coloration. J. S. C. I.

*Detection of chlorides and bromides in the presence of thiocyanates.* G. SPACU. *Bul. soc. Stiinta Cluj* 1, 302-5(1922).—Pyridine (8-10 drops) and excess of a neutral Cu sulfate soln. are added to a neutral soln. contg. thiocyanates, and after sepg. the ppt. of  $\text{CuPy}_2(\text{CNS})_2$  (cf. preceding abstr.), the soln. can be tested for chlorides and bromides by the usual methods.

J. S. C. I.

*Microchemical estimation of copper.* G. SPACU. *Bul. soc. Stiinta Cluj* 1, 296-301(1922).—The green compd. described previously (cf. preceding abstr.) is pptd. in a double sepg. funnel in which the upper and lower compartments hold 35 cc. and 5 cc., resp. After pptn., the soln. is shaken 3 times with 2 cc. of  $\text{CHCl}_3$  in the upper compartment, and the  $\text{CHCl}_3$ , after settling, is run into the lower compartment, whence it is drained into a porcelain crucible. The  $\text{CHCl}_3$  is evapd. *in vacuo* in a desiccator, and the ppt. is either weighed as  $\text{CuPy}_2(\text{CNS})_2$ , or is converted into  $\text{CuO}$  or  $\text{CuS}$  before weighing.

J. S. C. I.

*An examination of Rodillon's test for nitrites.* HENRY LEFFMANN. *Am. J. Pharm.* 95, 110-1(1923).—L. points out difficulties with the resorcinol test as described by Rodillon (*C. A.* 17, 1521).

W. G. GAESSLER

*The determination of carbonic acid.* K. K. JÄRVINEN AND O. SUMELIUS. *Z. anal. Chem.* 62, 223-9(1923).—Considerable difficulty was experienced in the rapid detn. of  $\text{CO}_2$  in carbonates. The most satisfactory method tried was the following. Place powder corresponding to about 0.5 g.  $\text{CO}_2$  in a 300-400-cc. Kjeldahl flask with about 100-150 cc. water. Through the stopper of the flask introduce a dropping funnel 40 cc. long so that the stem reaches only to the bottom of the stopper. Connect the flask through 50 cm. of glass tubing, with the bottom of a buret tube about 80 cm. long and 2 cm. in diam. In the buret tube place 50 cc. of  $N$   $\text{NaOH}$  soln. and protect it from  $\text{CO}_2$  in the air by a small soda-lime tube at the top. Boil the liquid in the flask, to which litmus and pumice were also added, till all air is expelled and then introduce about 25 cc. of 2  $N$   $\text{HCl}$  at the rate of 1-2 drops per sec. After the soln. in the flask has become acid, boil about 2 mins. longer. Pour the  $\text{NaOH}$  soln. into a flask, add about 50 cc. of  $N$   $\text{BaCl}_2$  soln. and titrate with  $N$   $\text{HCl}$  using phenolphthalein as indicator. Run a blank expt. and make a corresponding reduction in the analysis. If the original substance contains free  $\text{CO}_2$  or a bicarbonate, use  $\text{NaOH}$  soln. instead of water in the flask. The analysis requires about 30 min. and the results are accurate to within about 2 mg. of  $\text{CO}_2$ . If the substance contains sulfite, add a little 30%  $\text{H}_2\text{O}_2$  to oxidize it. The presence of a little sulfide has no effect.

W. T. H.

*Analysis of sodium perborate.* H. BURKARDT. *Chem.-Ztg.* 47, 6(1923).—Dissolve 2.5 g. of the salt in water, neutralize to methyl orange with a measured vol. of 0.5  $N$   $\text{HCl}$ , boil off any  $\text{CO}_2$  with the use of a reflux condenser, cool, add phenol-

phthalein, 10 cc. glycerol and 0.5 *N* NaOH until a red color is obtained. Then add 10 cc. more of glycerol and titrate with more NaOH continuing until the addn. of glycerol fails to decolorize the soln. From these 2 titrations it is easy to tell (a) whether all alkali is combined with boric acid, (b) whether the borate is all present as perborate and (c) whether other persalt is present.

W. T. H.

**The examination of ammonium sulfate.** R. WINDISCH. *Chem.-Ztg.* **47**, 189 (1923).—Dissolve 10 g. in hot water, filter and dil. to 1 liter. Take 25 cc., evap. to dryness on the water bath and toward the last add 5 cc. of alc. Dry at 110° and ignite to const. wt.

W. T. HALL

**Estimation of sodium hyposulfite.** ANON. *Chem. Trade J.* **72**, 224 (1923).— $\text{Na}_2\text{S}_2\text{O}_4$  reacts with  $\text{CH}_2\text{O}$  to form  $\text{NaHSO}_4 \cdot \text{CH}_2\text{O} \cdot 2\text{H}_2\text{O}$  and  $\text{NaHSO}_4 \cdot \text{CH}_2\text{O} \cdot \text{H}_2\text{O}$  in equal amts. Of these products, the former reacts with  $2\text{I}_2$  to form  $\text{NaHSO}_4 \cdot \text{CH}_2\text{O}$  and 4HI. Shake 10 g. of  $\text{Na}_2\text{S}_2\text{O}_4$  with 1 liter of water contg. 20 cc. of 40% formaldehyde. To 100 cc. of water add 20 cc. of the  $\text{Na}_2\text{S}_2\text{O}_4$  soln. and 50 cc. of 0.1 *N*  $\text{I}_2$  soln. After 2 min. titrate the excess with 0.1 *N*  $\text{Na}_2\text{S}_2\text{O}_4$  soln. An empirical correction of 1% allows for atmospheric oxidation in prep. the original soln. in a short-stemmed flask.

W. T. HALL

**Formic acid. I. Gravimetric determination of formic acid.** FR. AUERBACH AND H. ZEGLIN. *Z. physik. Chem.* **103**, 161-77 (1922).—The gravimetric detn. of  $\text{HCO}_2\text{H}$  by the Hg procedure has been improved by the use of Gooch or Munroe crucibles. For an exact detn. an excess of 12 mg.  $\text{HgCl}_2$  over the stoichiometric quantity is necessary for each cc. of the reduction soln. For the detn. of small quantities of the acid (under 20 mg.), one millimol. of HCl must be added to the reduction soln. to prevent the sepn. of basic salts; while for the detn. of quantities of acid under 5 mg. the addn. of NaOAc must be reduced from 3 to 1 g. A NaCl content of 10 mg. per cc. of the reduction soln. does not interfere with the detn., provided a requisite excess of  $\text{HgCl}_2$  is present. Larger quantities of NaCl introduce errors. The disturbing influence of salicylic acid in the detn. can be reduced by small quantities of NaCl, if 1 millimol. of HCl is added simultaneously. Formic acid can be removed from its  $\text{Et}_2\text{O}$  solns. by extrn. with an aq. soln. of NaOAc, and its amt. in this detd. The modified procedure is as follows: Neutralize the soln. in an Erlenmeyer flask with  $\text{Na}_2\text{CO}_3$  or HCl if necessary. In case the soln. is strongly alkaline, pure AcOH must be used. To the neutral soln. add 1 cc. of *N* HCl and 3 g. of AcONa. If more than 0.1 g. of  $\text{HCO}_2\text{H}$  is present increase the NaOAc and if less than 5 mg. are present use only 1 g. Add 5%  $\text{HgCl}_2$  soln. (free from NaCl) so that 12 times as much is present as  $\text{HCO}_2\text{H}$  and, in addn., 12 mg. excess for each cc. of liquid. The total vol. should be kept between 50 and 100 cc. unless large quantities of  $\text{HCO}_2\text{H}$  are present. If salicylic acid or similar acid is present, add about 1 mg. NaCl for each cc. of soln. Cover the flask with a watch glass and heat on water bath for 2 hrs. with the bath boiling strongly and the vapors coming in contact with all of the outside surface of the flask. Filter through a Munroe or Gooch crucible, wash the  $\text{Hg}_2\text{Cl}_2$  with warm water and finally with alc. Dry at 100° for 1 hr. and multiply the wt. of  $\text{Hg}_2\text{Cl}_2$  by 0.09745 to get the wt. of  $\text{HCO}_2\text{H}$ . To clean the crucible, remove most of the ppt. with a fine brush and volatilize the remainder. To det.  $\text{HCO}_2\text{H}$  from ethereal solns. it is usually sufficient to run the soln. from a pipet under a soln. of NaOAc but if considerable  $\text{HCO}_2\text{H}$  is present it is desirable to shake the ethereal soln. in a separatory funnel with several portions of AcONa soln.

H. J. C.

**The determination of various monohydric phenols by the phenol reagent of Folin and Denis.** CARLETON HENNINGSEN. *Ind. Eng. Chem.* **15**, 406-7 (1923).—Studies of the phosphotungstic-phosphomolybdic acid reagent of F. and D. with  $\beta$ -naphthol, *m*-cresol, thymol isomylphenol, ethylphenol and butylphenol show that the color produced with the reagent fulfills most of the requirements of a colorimetric method.

With monohydric phenols in pure aq. solns. the intensity of the color appears to be proportional to the mol. concn. of the phenol so that the use of empirical factors is unnecessary in working with different phenols.

W. T. HALL

**Colorimetric determination of the water content of absolute alcohol.** I. M. KOLYHOFF. *Pharm. Weekblad* 60, 227-31(1923).—The sensitivity of azo indicators, e. g., methyl orange, to acid diminishes with increasing EtOH concn. of the medium. Representing the sensitivity quotient in H<sub>2</sub>O by 1, there is an increase to 135 in 91.5% EtOH, then a decrease to 23 in 99.3% EtOH. The method is based upon the matching of colors of an aq. and an alc. soln. of the indicator. Three reagents are required: (a) a satd. soln. of methyl orange in strong EtOH, (b) 0.01 N HCl in H<sub>2</sub>O, (c) 0.1 N HCl in strong EtOH (from EtOH and HCl gas). In a tall cylinder place 25 cc. H<sub>2</sub>O, add 0.1 cc. of soln. a and 0.4 cc. of soln. b. The intermediate orange-red color of the indicator is obtained. In a 2nd cylinder place 25 cc. of the EtOH to be tested, add 0.12 cc. of soln. a, then soln. c from a Bang buret until the color is the same as in the 1st cylinder. Note the temp. of the alc. soln. For concns. between 99.7% and 95.0% and temps. above 15° interpolations may be made from the following table,—

EtOH vol. %.	0.1 N alc. HCl to match color of aq. soln. cc.	Correction for each degree above 15.
99.7	0.21	0.007
99.0	0.96	0.03
98.0	2.27	0.07
97.0	3.45	0.10
96.0	4.30	0.12
95.0	5.05	0.13

A. W. DOX

**Analytical applications of the reaction between sulfites and aldehydes.** JOSÉ ESTALELLA. *Anales soc. españ. fis. quim.* 20, 271-82(1922).—A 1% soln. of Na<sub>2</sub>SO<sub>3</sub> in the presence of phenolphthalein is proposed as a reagent for aldehydes. Similarly, HCHO in the presence of phenolphthalein may be used as a reagent for sulfites. In both cases the reaction consists in the formation of an aldehyde-bisulfite compd. with liberation of NaOH and the development of a pink color in the soln. Cf. following abstr.

L. E. GILSON

**The action of aldehydes on mixtures of sulfites and bisulfites.** JOSÉ ESTALELLA. *Anales soc. españ. fis. quim.* 20, 437-40(1922).—The effects of temp. and concn. on the reaction described in the above abstract are discussed. When the soln. to be tested is cold and only a little of the reagent is added, several minutes may be required for the pink color to develop, but by adding a large amt. of reagent and warming, the reaction may be made almost instantaneous. CO<sub>2</sub> interferes a little. NaHSO<sub>3</sub> mixed with the Na<sub>2</sub>SO<sub>3</sub> makes the reaction slow and uncertain.

L. E. GILSON

**Application of the Devarda method to the determination of nitrogen in nitrocellulose.** A. KOEHLER, M. MARQUEYROL AND P. JOVINET. *Mém. poudres* 19, 348-50 (1922).—Moisten 0.7 g. nitrocellulose with a little EtOH in a 700-cc. flask, add 30 cc. H<sub>2</sub>O<sub>2</sub> (12% soln.), 60 cc. H<sub>2</sub>O and 50 cc. KOH soln. (sp. gr. 1.3), cover the flask loosely and heat on a water bath at 50-60° with frequent shaking. The substance should dissolve without coloring the liquid yellow. Heat over a free flame until evolution of gas ceases, and finally cool to room temp. Add 5 cc. 95% EtOH, 2.5 g. Devarda alloy (Al 45, Cu 50, Zn 5) finely pulverized and screened (25 mesh per cm.), and connect the flask with a Wagner distn. tube whose tip is immersed in 25 cc. N/3 H<sub>2</sub>SO<sub>4</sub> and 50 cc. H<sub>2</sub>O in a flask. After H<sub>2</sub> has evolved for 15-20 min., apply gentle heat for 10 min. to complete reduction and finally distill off most of the liquid during 30-35 min. Titrate the excess H<sub>2</sub>SO<sub>4</sub> with N/5 NH<sub>4</sub>OH soln., using methyl red in EtOH soln. (0.1%)

as indicator. A blank test with reagents usually gives a correction of about 0.4 cc.  $N/5 \text{ NH}_4\text{OH}$ . Results on  $\text{KNO}_3$  and nitrocellulose show the method to be accurate to about 0.3% N. C. G. STORM

**Determination of nitrogen in nitrates and in nitrocellulose.** A. KOEHLER, M. MARQUEYROL AND P. JOVINET. *Mem. poudres* 19, 351-5(1922).—A description of the details of the method and app. (see preceding abstract), as applied to the detn. of both ammoniacal and nitrate N. In the case of *smokeless powder* the nitrocellulose is pptd. from soln. as in the detn. of solvent, the ppt. washed with  $\text{CHCl}_3$  and dried before detn. of N. C. G. STORM

**Determination of nitrogen in nitroglycerin.** A. KOEHLER, M. MARQUEYROL AND P. JOVINET. *Mem. poudres* 19, 356-8(1922).—The modified Devarda method described in the 2 preceding abstracts may be applied to smokeless powders contg. nitroglycerin if the sample is sufficiently finely divided. To obtain satisfactory results on pure nitroglycerin or on exts. contg. the latter, 0.5 g. of the liquid sample is sapond. in a 100-cc. conical flask at  $35-40^\circ$  by a mixt. of KOH soln. and  $\text{H}_2\text{O}_2$ , while being well agitated (1500 r. p. m.) with a glass agitator, on the stem of which are blown 2 bulbs which partly close the neck of the flask and prevent loss from splashing. After 40 min. the liquid is transferred to the flask of the reduction app., treated with the Devarda alloy and distd. Pure nitroglycerin contg. 18.51% N (theory) gave 18.42-18.48% N. C. G. STORM

**The determination of nitric oxide.** A. KOEHLER AND M. MARQUEYROL. *Mem. poudres* 19, 359-61(1922).—The method of Baudisch and Klinger (*C. A.* 7, 951) for detn. of NO in gas mixts. has been modified by the use of  $\text{C}_6\text{H}_5\text{NH}_2$  for absorbing the  $\text{N}_2\text{O}_3$  resulting in the 1st stage of oxidation of NO. Eighty cc. of the gas, measured over Hg, is treated with 0.6 g.  $\text{C}_6\text{H}_5\text{NH}_2$  and sufficient O to leave about 5 cc. excess after reaction with the NO.  $\text{CO}_2$  is absorbed in KOH, the excess O in alk. pyrogallate, and the remainder of the analysis conducted as usual. The method was used for the analysis of NO obtained in the nitrometer or in the Schloessing app. A high degree of accuracy was obtained in analysis of known mixts. C. G. STORM

**Formic acid. II. Partition of formic acid between water and ether and its analytical applications (AUERBACH, ZEGLIN) 2.**

BARRAL, E.: *Analyse chimique qualitative*. 2nd Ed. Paris: J. B. Baillière et fils. 735 pp. Fr. 26.

CLASSEN, ALEXANDER: *Handbuch der analytischen Chemie*. II. Stuttgart: F. Enke. 361 pp.

ENKLAR, C. J.: *Handleiding bij de kwalitatieve analyse ten dienste der burger-scholen*. Groningen: P. Noordhoff. 48 pp.

**Sampling wet clays, ores, or other sticky materials.** F. M. MARTIN. U. S. 1,448,758, Mar. 20. A compact stream of the material uniformly and continuously falling in the air is disintegrated as it falls and small samples are taken from it at intervals and mixed with each other.

## 8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND EDW. F. HOLDEN

**The development of mineralogical methods.** T. L. WALKER. *Am. Mineral.* 8, 41-6(1923).—Presented chronologically, the methods which have been developed for mineralogical research and description are: the Wernerian (use of the more obvious



phys. properties); geometrical (crystal form); chem.; petrographic (microscopic study of transparent minerals); synthetic (artificial production of minerals); mineralographic (microscopic study of opaque minerals); and the method of Friedel and Laue (X-ray detn. of cryst. structure). E. F. H.

The constitution of the titaniferous magnetites from Pretoria District. H. R. ADAM. *J. S. African Chem. Inst.* 6, 3-7 (1923).—Magnetite from Pretoria had 30% ilmenite. Expts. on the reduction of the ore by heating it in H are described. The Fe of ilmenite is not as easily reduced as that of the simple Fe oxides, which is against the view that the constitution of ilmenite is  $\text{Fe}_2\text{O}_3 \cdot \text{Ti}_2\text{O}_3$  instead of  $\text{FeO} \cdot \text{TiO}_2$ . After reduction the Ti is present as  $\text{Ti}_2\text{O}_3$ . This ore is peculiar in that at certain positions of a magnet the particles are repulsed. This property, as well as the ordinary magnetism, is destroyed by heating the material in air. E. F. H.

Parsonsite, a new radioactive mineral. A. SCHOER. *Compt. rend.* 176, 171-3 (1923).—This new mineral, named in honor of Prof. A. L. Parsons (Toronto), is from Kasolo, Katanga, Belgian Congo. It is associated with torbernite, as an earthy, pulverulent, sometimes compact, mass. It is in minute crystals of pale brown color and greasy luster. Under the microscope these are found to have almost colorless and transparent edges, while the interior contains very small brown grains, from which the color is probably derived. The minute crystals are prismatic lamellas;  $(100) \wedge (001) = 81^\circ$ ,  $(100) \wedge o = 47-8^\circ$ ,  $(001) \wedge o = 28-9^\circ$ . They are weakly birefringent, the extinction is inclined  $12^\circ$  to the elongation, which is  $+$ ;  $n > 1.99$ . Biaxial, either monoclinic or triclinic. Sp. gr. = 6.23 ( $17^\circ$ ). Streak is very pale brown, with rose tinge. In the closed tube, water is given off and the mineral becomes yellowish. On charcoal it fuses to a black globule, and is easily sol. in acids. In  $\text{HNO}_3$  there was a slight residue containing  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ . The solutions react for Pb, U, and P. Analysis gave:  $\text{H}_2\text{O}$  1.56, PbO 44.71, CuO 0.25,  $\text{UO}_2$  29.67,  $\text{P}_2\text{O}_5$  15.08, TeO<sub>2</sub> 3.01,  $\text{MoO}_3$  0.43, CaO 0.63,  $\text{Al}_2\text{O}_3$  1.23,  $\text{CO}_2$  1.19,  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  (insol.) 1.51, sum 99.47 (99.27%). The CuO comes from a little torbernite present as an impurity. The formula is:  $2\text{PbO} \cdot \text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . The mineral is radioactive. E. F. H.

The genesis of diamond. ST. J. THUGUTT. *Rev. sci.* 61, 97-102 (1923).—A review. E. F. H.

Origin of coals. E. DONATH AND A. LISSNER. *Brennstoff-Chem.* 3, 231-7 (1922).—The current chem. and geological theories of coal formation are critically reviewed. The theory of the transformation of wood and peat through lignites to coal and anthracite is being modified. Coal is not to be regarded as necessarily derived from peat as found in recent deposits and from brown coals such as exist now. That the brown coals and coal result from different kinds of vegetable matter is a view supported by the authors. They accept the Fischer-Schrader theory of the formation of coal from lignin (*C. A.* 15, 1610; 16, 2099, 2975), the cellulose being destroyed by bacterial action, but the theory is regarded as incomplete in ignoring the vegetable and animal proteins. The proportion of N in coal is such as to imply the existence of considerable quantities of these. There is some evidence of the possibility of union of protein with cellulosic matter, which would then be preserved. The true coals and harder lignites have probably passed through a pressure distn. process as described by Bergius (cf. *C. A.* 8, 1004). J. S. C. I.

The theory of petroleum. D. MILSOM. *Queensland Govt. Mining J.* 23, 394-7, 436-8, 481-3 (1922).—The existing theories of the origin of petroleum are reviewed, giving references to the literature; the relation of shale-oil residues to other bitumens is discussed; and the theories of accumulation of oil and gas are outlined, with discussion of oil-bearing geological formations, and favorable and unfavorable signs in petroleum areas. A. BURTS

The origin of salt domes. A. G. WOLF. *Eng. Mining J.-Press* 115, 412-4(1923).—A chronological tabulation of theories thus far advanced. E. H.

The composition of bitters in pans in the Cape Province. G. J. R. KRIEG. *J. S. African Chem. Inst.* 6, 8-10(1923).—Analyses of 9 bitters are given. The Darling bitters have high salinity, are distinctly alk., with much Mg. They contain traces of Br and I, which appears to indicate a marine origin for the salt pans. E. F. H.

The present status of geologic research. The structure of the earth's crust. E. BEDEKER. *Naturwissenschaften* 11, 123-8(1923).—A general discussion. C. C. D.

JAEGER, F. M.: Vulkanische actie en rotsvorming als chemische problemen. Groningen, Haag: J. B. Wolters. 27 pp.

### 9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The metallurgy of tin and its latest development. T. K. VAN GÛLDER. *De Ingenieur* 38, 125-30(1923).—On the island of Banka in the Dutch Indies the tin ores are found 6-20 m. under the ground. The ores are washed, to remove sand or lighter impurities, and reduced with charcoal in blast furnaces. Expts. with flame-furnaces have not been successful. R. BEUTNER

Progress in cyanidation. ANON. *S. African Mining Eng. J.* 33, 631-2(1923).—Practice at several of the newest plants is outlined. The Crowe vacuum process and Merrill Zn-dust pptn. are almost invariably included, and Zn-dust pptn. is superseding Zn boxes at many older plants. A. BUTTS

The cyanide plant of the Nurupi mines, Korea. CHARLES FLURY. *Eng. Mining J.-Press* 115, 579-80(1923).—Flow sheets and extn. costs are given. E. H.

The use of sodium peroxide in cyanidation at the Teck-Hughes gold mine. D. L. H. FORBES. *Eng. Mining J.-Press* 115, 440 1(1923).—Introduction of  $\text{Na}_2\text{O}_2$  increased extn. 6.5% at this mine at Kirkland Lake, Ont. The ore has part of its Au as telluride, requiring very fine grinding and intense oxidation. The amt. of  $\text{Na}_2\text{O}_2$  added is from 0.4 to 1.0 lb. per ton of ore, depending on the Au content. For \$20 to \$30 ore the extra milling cost is 12 to 18 c. per ton, while the increased recovery is 50 c. to \$1 per ton. A flow sheet is given. A. BUTTS

Gold, silver, copper, lead and zinc in Colorado in 1921. C. W. HENDERSON. U. S. Geol. Survey, *Mineral Resources of U. S., 1921*, Pt. I, 479 511 (Preprint No. 28, published Mar. 16, 1923). E. H.

Gold, silver, copper, lead and zinc in New Mexico and Texas in 1921. C. W. HENDERSON. U. S. Geol. Survey, *Mineral Resources of U. S., 1921* Pt. I, 467-77 (Preprint No. 27, published Mar. 15, 1923). E. H.

Short method for figuring alloys. J. M. QUINN. *Blast Furnace and Steel Plant* 11, 232-8(1923).—Calcs. and tables are given for the production of alloy steels. E. H.

Titanium. A. H. A. ROBINSON. Can. Dept. Mines, *Mines Branch* No. 579, 127 pp.(1922); cf. *C. A.* 17, 948.—A review giving the history and properties of Ti and its compds., metallurgy of Ti, its occurrence in Canada, production statistics and uses. E. H.

The metallurgical aspect of the production of cold. COSMO JOHNS. *Trans. Faraday Soc.* 18, 259-61(1922).—A retrospect. Refrigeration offers possibilities as a means of obtaining O-enriched air, and this in turn would greatly benefit the steel, copper and allied industries. W. H. BOYNTON

An accurate method of determining the hardness of metals with particular reference to those of a high degree of hardness. R. L. SMITH AND G. E. SANDLAND. *Proc.*

*Inst. Mech. Eng.* 1, 623-41(1922).—By a suitable modification of the Brinell formula it is possible to obtain truly relative hardness figures from which may be calculated the load required to give a const. impression. The authors have calibrated natural pyramidal diamonds to replace the steel ball and so obtain substantially correct values for hardness for the higher ranges. The load applied with the diamond test is light and the impression shallow, and the test is very sensitive therefore to the surface hardness of the material. A more accurate est. of the max. stress is possible with the modified hardness numbers, as they lie on a straight line which passes through the origin, and only one conversion factor (0.23) is required over the range 30-90 tons for plain C steels. J. S. C. I.

**Analysis of alloys by the aid of specific heats.** K. ZAHLBRUCKNER. *Chem.-Ztg.* 46, 637-8(1922).—The proportion of 2 metals, of known sp. heats, in an alloy may be found by detg. the sp. heat of the alloy by means of the usual water calorimeter, the value found being equal to the sum of the products of the % of each constituent present and its sp. heat. In the case of a ternary alloy the proportion of one constituent must be found by chem. analysis, or, assuming that the sp. gr. of the constituents is also known, by detg. the sp. gr. of the alloy and plotting two equations. To obtain results to 1% by this method the temp. measurements must be made in hundredths of a degree. Examples and graphs are given. J. S. C. I.

**Primary and secondary recrystallization of tin.** G. MASING. *Wiss. Veröffentl. Siemens-Konzern.* 1, [3] 31-4(1922).—In the case of tin, M. shows experimentally that the secondary crystn. following a secondary deformation is characteristic of that deformation and does not take place if the metal, after casting, is subjected to a similar deformation without being subjected to a primary deformation (cf. *C. A.* 16, 3857). Thus, a sheet of tin which, after being cast, was pierced, and then subjected to recrystn., showed a ring of comparatively small crystals around the hole, whereas a similar sheet that had been rolled before piercing showed, after recrystn. at the same temp., extremely large secondary crystals spread evenly around the hole and gradually merging into the original primary crystals. J. S. C. I.

**Occurrence of ferrite-graphite eutectic in certain kinds of cast iron.** E. SCHTZ. *Stahl u. Eisen* 42, 1135-6(1922).—A cast iron of the following compn.: graphite 3.22, combined C 0.38, Si 3.31, Mn 0.88, P 0.89, and S 0.104%, showed a large amt. of graphite-ferrite eutectic surrounding well defined ferrite polygons and pearlite crystals, while free graphite flakes were evenly distributed throughout the mass. The iron had a Brinell hardness no. of 150 and good mech. properties, and could be readily machined. The structure was probably produced in the following manner: on cooling from 1240° to 1152° mixed crystals are pptd. which become slowly enriched in C, viz., from 0.8 to 1.3%. At 1152° the ferrite-graphite eutectic with 4.5% C freezes out, while at the same time in the regions of pure pearlite the mass cools according to the metastable Fe-Fe<sub>3</sub>C system in which between 1240° and 1145° mixed crystals with 0.8-1.7% C sep., followed by freezing of ledeburite at 1145°. Eventually the latter decomposes between 1145° and 1090° into free graphite and pearlite. J. S. C. I.

**Lath breakdown tests of some high-speed tool steels.** H. J. FRENCH AND JEROME STRAUSS. *Bur. Standards, Tech. Papers* No. 228, 183-225(1923).—See *C. A.* 16, 3847. E. J. C.

**Stainless steel—Its properties and some of its engineering applications.** J. H. G. MONYPENNY. *Iron Coal Trades Rev.* 106, 342-3(1923); cf. *C. A.* 16, 229. J. L. WILEY

**Physics of cast iron and its bearing on all cast-iron products and specifications for cast iron.** WM. R. WEBSTER. *Proc. Am. Soc. Testing Materials* 22, 11, 217-23 (1922).—See *C. A.* 17, 955. E. J. C.

**An investigation of the properties of chilled-iron car wheels.** II. Wheel fit,

static load, flange pressure-strains and ultimate strength of flange. J. M. SNODGRASS AND F. H. GÜLDNER. Univ. Ill. Eng. Expt. Sta., *Bull.* 134, 63 pp.(1922); cf. C. A. 16, 2662.—An exptl. study of the ability of the plates of the wheel to withstand internal stress due to flange pressure. The app. consisted of a 200-ton hydraulic jack acting at right angles to the flanges, supported on rolls which in turn were carried on the bed of a 600,000-lb. testing machine. Strains due to the various combinations of load were measured with a Berry strain-gage. The application of the normal static load of service does not materially alter the strains already present on the outer face through mounting. On the inner face the bending of the curved plate in the core region becomes pronounced. The combined effect of mounting, static load and flange pressure approximating the max. in service results in tensile strains in both radial and tangential directions in the outer face, the max. occurring near the junction of the inner and outer plates in a radial direction. These combined strains are not serious in themselves, but if to them are added the strains of severe and prolonged brake applications the results might lead to cracks and failures. With regard to the flange strength of chilled-iron wheels this may be increased to meet any future service requirements by a proper placing of additional metal in the tread and flange. III. Strains due to brake application, coefficient of friction and brake-shoe wear. *Ibid* 135, 97 pp.(1923).—The strains produced by brake application were detd. in one steel and six chilled-iron wheels at speeds ranging from 10 to 50 mi. per hr., brake-shoe pressures from 1000 to 3000 lbs. and lengths of run from 10 to 30 miles. Data were also obtained from detn. of coeff. of friction, tangential pull, work done by the brake-shoe and metal lost by the shoe. Stresses set up by temp. gradients due to brake application are transmitted mainly through the outer plates. At slow speed, temp. gradients are small because of conduction and radiation effects with the result that temp. deformations form a large part and strain a small part of total deformation. Stresses resulting from temp. gradients may be kept within safe limits by the use of cooling periods or cooling stations. When subjected to severe brake application and no other stress-producing influences a wheel has its position of max. stress consistently located at a definite position, which may not correspond to the position of min. strength as indicated by service failures. Prolonged and heavy brake application may cause strains of sufficient intensity to crack either chilled-iron or steel wheels.

H. I. OLIN

Case-hardening plant of the Timken Roller Bearing Co. E. W. EHN. *Chem. Met. Eng.* 28, 578-87(1923).

E. H.

Modification of the powder method of determining the structure of metal crystals (OWEN, PRESTON) 2.

BUCHNER, GEORG: *Das Atzen der Metalle und das Färben der Metalle*. 3rd revised edition. Berlin: M. Krayn. 207 pp.

LENN, PH.: *Materialienlehre mit einleitenden chemischen Grundbegriffen für Metallberufe*. 3rd ed. revised. Stuttgart: Holland & Josenhans. 63 pp.

VICKERS, CHARLES: *Metals and Their Alloys*. New York: H. C. Baird. 767 pp.

WÜST, FRITZ: *Legier- und Lötkunst*. 8th revised ed. Leipzig: Bernh. Friedr. Voigt. 160 pp. M 100.

Adhesive coating for ore-receiving surfaces. R. LUCKENBACH. U. S. 1,448,927, Mar. 20. Surfaces such as vanner belts for the retention of minerals which are to be sepd. from associated gang are coated with a mixt. of petroleum grease and a rubber soln. U. S. 1,448,928 relates to the concn. of ores by this method.

Ore concentration by flotation. R. LUCKENBACH. U. S. 1,448,929, Mar. 20.

Ore is mixed with  $H_2O$  and the pulp thus formed is subjected to aeration flotation after treatment with reaction products of coal tar, coal-tar creosote, acetone or other solvent and  $NaOH$ .

**Reducing and roasting ores.** E. FLEISCHER. U. S. 1,448,340, Mar. 13. A shaft furnace is used, through successive sections of which the material descends in the form of inverted conical masses. Reducing gas is passed through the lower part of the mass, most of the reducing gas is withdrawn at the upper end of this portion, the remainder of the reducing gas is drawn through the next portion and fired at its upper part and the fired gas is drawn through a superposed portion of the ore mass.

**Separation of ore pulp constituents.** W. O. BORCHERT. U. S. 1,448,514, Mar. 13. Removal of colloidal constituents is facilitated by a preliminary deflocculation of flocculated colloidal substances in the ore pulp.

**Mineral separation.** W. O. BORCHERT. U. S. 1,448,515, Mar. 13. Mineral pulps contg. colloidal material are subjected to a deflocculating treatment before fine grinding to effect a sepn. of colloidal constituents after the latter have been dispersed or deflocculated and are then subjected to a further sepn. which would be interfered with by the colloidal constituents if they had not been previously removed.

**Apparatus for hydraulic mineral separation.** E. D. MERWIN. U. S. 1,448,310, Mar. 13.

**Vanadium from ores.** P. A. MACKAY. U. S. 1,450,507, Apr. 3. Ores such as those contg. oxides of V and Ph are treated with fuming  $H_2SO_4$  and  $V_2O_5$  is reduced to  $V_2O_3$  by  $SO_2$  to obtain vanadyl sulfate. The soln. is subsequently dild. with  $H_2O$  to ppt. other materials and leave the V in soln.

**Removing phosphorus compounds from iron ores.** TORAO TAKAGI and the NIPPON DENKI SEITETSU KABUSHIKI KAISHA. Japan. 40,524, Nov. 7, 1921. A mixt. of powdered Fe ore 1 and 1-2%  $NaOH$  soln. 1 part is boiled for 30 min. under agitation. When the mixt. was cooled, the ore is sepd. from the soln. and washed. P in the ore is changed into  $Na_2HPO_4$ .

**Blast furnace.** G. L. SHOOK. U. S. 1,448,772, Mar. 20. A stock-line section of the furnace is faced with metal lining units with cavities filled with burned clay or similar material.

**Spelter furnace.** D. B. JONES. U. S. 1,450,161, Mar. 27. The furnace comprises a heating chamber the sole or hearth of which is formed of spaced longitudinally extending walls, the upper edges of which form guides for the material to be treated, e. g., Zn ore briquets, and connections for discharging heated gases into the spaces between the walls.

**Rabbit furnace adapted for roasting ores.** H. C. HOLTHOFF. U. S. 1,450,900, Apr. 3.

**Iron-purifying and balling furnace.** O. S. PULLIAM. U. S. 1,449,546, Mar. 27. A puddling furnace comprises a rotary hearth and an agitator movable in a circular path over the hearth and in contact with its surface.

**Furnaces adapted for heating metals or glass.** J. P. SNENDON. U. S. 1,448,160-1-2-3, Mar. 13.

**Stationary horizontal furnace or oven adapted for heating glass, metals or ores.** P. R. CASSIDY. U. S. 1,448,194, Mar. 13.

**Carbon steel.** C. CUMINGS. U. S. 1,449,657, Mar. 27. A C steel, the elastic limit of which is at least 80% of its tensile strength, is prepd. by subjecting molten steel to the effects of an explosion, violent agitation and rise of temp.

**High-speed steel containing no tungsten.** W. L. E. EULENDER. U. S. 1,448,288, Mar. 13. A steel of high cutting capacity is formed with a content of C 0.5-0.8, Mo 6-10, Cr 2-8, Mn 0.2-0.4, Si 0.2-0.4 and V 0.15-2%.

**Melting and deoxidizing iron or steel.** A. E. GREENE. U. S. 1,449,319, Mar. 20. Fe or steel is melted on a basic hearth with an oxidizing slag, the slag is removed and the bath is treated with a finishing slag comprising lime and silica in approx. such proportions as to form a neutral mixt.

**Automatic electric apparatus for manufacture of iron briquets.** YOHJI YAMAGUCHI and TOSHIMASA TAKEBE. Japan. 40,539, Nov. 7, 1921. Structural features.

**Reclaiming spent pickling solutions.** H. S. MARSH and R. S. COCHRAN. U. S. 1,450,216, Apr. 3. Spent pickling soln. contg.  $\text{FeSO}_4$  is passed through a looped circuit in which the return branch is confined within heat-conducting walls submerged in the outgoing branch, and the stream is cooled sufficiently to effect crystn. of  $\text{FeSO}_4$ . U. S. 1,450,217 relates to an app. for reclaiming spent pickling solns. by similar treatment.

**Refining the grain of seamless drawn metal tubes.** A. C. MORSE and H. R. LEWIS, JR. U. S. 1,450,699, Apr. 3. Heat treatment and quenching are used to produce the desired grain of the metal.

**Heat treatment to render tungsten ductile.** E. ROTH. U. S. 1,450,734, Apr. 3. A rod or long ingot of non-ductile W is passed slowly through a short heating zone having a temp. equal to or above the crit. temp. at which the cryst. structure of the W permanently changes while that part of the rod or ingot which has not reached this heating zone is kept cool.

**Compacting difficultly fusible metals.** YOSHIO NAKAZAWA and DENJI OKADA. Japan. 40,504, Nov. 4, 1921. Powdered metals, such as W, Mo, U, Cr, etc., are compacted and made ductile by heating with the N compd. of the metal and  $\text{Ca}(\text{NO}_3)_2$  under pressure. E. g., 300 g. of purified W powder in a flat Pt or Ni vessel is heated at  $900\text{--}1,000^\circ$  in a gas muffle furnace for 8–10 hrs., while dried  $\text{H}_2$  and  $\text{NH}_3$  are passed at velocities of 2 and 1.4 cu. ft. per hr., resp. The fine granules of the material are changed into the N compd. After cooling in the furnace, the product is mixed thoroughly with about 0.3%  $\text{Ca}(\text{NO}_3)_2$  and pressed in a steel mold under 20–30 tons per sq. in. The block is then heated in a muffle furnace at  $1000^\circ$ , in a current of 6 cu. ft. per hr. of  $\text{H}_2$ ;  $\text{Ca}(\text{NO}_3)_2$  acts as a flux. On heating the furnace to  $1400\text{--}1500^\circ$ , the N compd. decomposes into metallic W. After 3–5 hrs., the temp. is lowered to  $800\text{--}1000^\circ$  and a mixt. of  $\text{H}_2$ , 6 cu. ft. per hr., and  $\text{NH}_3$ , 2 cu. ft. per hr., is passed for about 10 hrs., during which only coarse powder is changed into the N compd. Then the temp. is raised to  $1500^\circ$  in the presence of  $\text{H}_2$  to decomp. the N compd. If the product is not homogeneous, the process is repeated.

**Aluminum alloy.** C. PACK. U. S. 1,449,052, Mar. 20. An alloy which is suitable for making die castings is formed of Al 85% or more, Ni 3–6%, Cu 3–6% and Si 1.5–4%.

**Copper alloy.** A. O'ROURKE. U. S. 1,448,571, Mar. 13. An alloy which is adapted for valve casings and other plumbing fixtures is formed of Cu 55–65, Zn 8–20, Ni 10–25, Pb 3–10, Sn 1–5, Sb 0.5–2 and Fe 0–2%.

**Gold-palladium-platinum alloy.** C. S. VIDEON. U. S. 1,449,154, Mar. 20. An alloy which is adapted for dental use as a Pt substitute is formed of Au 49, Pd 37 and Pt 14 parts.

**Iron-silicon alloy.** W. J. BECK and J. A. AUPPERLE. U. S. 1,449,373, Mar. 27. An alloy which may be worked by rolling or forging and which is resistant to corrosion under atm. exposure and is adapted for manuf. of roofing, smoke stacks, flumes and pipes is formed mainly of Fe and Si which serves to induce the formation of  $\text{Fe}_3\text{O}_4$  on the surface of the metal and protect it from corrosion.

**Tool alloy containing cobalt, tantalum and a chromium-group metal.** F. T. MCCURDY. U. S. 1,449,338, Mar. 20. An alloy which is adapted for making cutting tools is formed of Co 50, Cr 25, W 15 and Ta 1–5 parts with small amts. of C and Si.

Alloy molds for casting metals. H. A. MYERS. U. S. 1,450,186, Apr. 3. An alloy contg. Ni 5-15 and Fe 85-95 (with or without Mn 1-2%) is used in making molds for casting ferrous metals. The mold may be machined and preferably is coated with Zn.

Magnet cores for loading coils. B. H. JACKSON. U. S. 1,449,542, Mar. 13. A magnet core is demagnetized while its permeability is unstable and then baked until its magnetic properties are rendered stable.

Welding copper to iron. G. R. TREMOLADA. U. S. 1,449,637, Mar. 27. Cu associated with an Fe alloy is placed in a mold and molten Fe is poured into the mold so as to effect an integral fused union with the Cu. Cu fins may be thus united to cast-Fe cylinders for air-cooled internal-combustion engines.

## 10—ORGANIC CHEMISTRY

CHAS. A. ROULLER AND CLARENCE J. WEST

The oxidation of paraffin by means of atmospheric oxygen. AD. GRÜN AND F. ULBRICH. *Z. angew. Chem.* 26, 125-6 (1923).—By means of the app. previously described (Grün and Wirth, *C. A.* 15, 1071), it is shown that the yield of acids from paraffin by oxidation with a current of air at 160° increases with the quantity of air that is passed through the app. The yield also increases with the time of oxidation. Traces of H<sub>2</sub>O in the air have a beneficial effect, while CO<sub>2</sub> in the air retards oxidation. T. S. C.

The calcium carbide inquiry. WM. J. POPE. *Chemistry and Industry* 42, 5-7, 117-20, 169-72 (1923).—Org. chemistry is defined, and it is proved that CaC<sub>2</sub> is an org. chemical. T. S. CARSWELL.

Chemical and pharmacological relations of unsaturated radicals. IV. J. V. BRAUN AND W. SCHIRMACHER. *Ber.* 56B, 538-48 (1923); cf. *C. A.* 17, 1083.—In its chem. and pharmacol. properties the  $\beta$ -butenyl radical is very similar to the allyl radical. From MeCH:CHCHO was prepd. MeCH:CHCH<sub>2</sub>Br (A) through the alc. A treated with Mg in abs. Et<sub>2</sub>O gave hi- $\beta$ -butylene. With PhMgBr it gave  $\beta$ -butenylbenzene and a like butenyl compd. when treated with *p*-bromoanisole. On hydrogenation *p*-butylanisole resulted.  $\beta$ -Butenyl Ph ether on heating rearranges to *o*- $\beta$ -butenylphenol. PhNMeCH<sub>2</sub>CH:CHMe reacts with BrCN to form PhNMeCN and A. MeCH:CHCH<sub>2</sub>SCN rearranges to MeCH:CHCH<sub>2</sub>N:CS. All these reactions are like those of analogous allyl compds.  $\beta$ -Butenylhomocholine, m. 52°, strongly hygroscopic, is prepd. from HOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> and A in C<sub>6</sub>H<sub>6</sub>.  $\beta$ -Butenylfluorocodine, from norcodeine and A, sol. in all solvents, softens above 40°, m. 44°; hydrochloride shows but slight tendency to cryst.; picrate, yellow flocks, sol. in alc., m. 128°; platinum salt, bright yellow powder, sol. in hot H<sub>2</sub>O, decomps. 198-200°. Diethyl dibutenylmalonate, from 2 mols. A added to 2 atoms Na in alc. and 1 mol. CH<sub>3</sub>(CO<sub>2</sub>Et)<sub>2</sub>, b<sub>17</sub> 152-4°. Heated with urea and Na in alc. at 100° for 6 hrs. in a sealed tube it gives C,C-di- $\beta$ -butenylbarbituric acid, white platelets, m. 108°; soly. in cold H<sub>2</sub>O 1.5 g. per l., in boiling H<sub>2</sub>O, 5 g. per l. Sodium salt, easily sol. in H<sub>2</sub>O; bromine addition product, m. 195°, difficultly sol. in Et<sub>2</sub>O, almost insol. in petr. ether. The pharmacol. action of these compds. will be described in another place. F. A. CAJORA.

Synthesis by means of magnesium allyl halides. SAMUEL COPPEY. *Rec. trav. chim.* 41, 652-4 (1922).—Allyldimethylcarbinol (A) was first obtained by Saytzev (*Ann.* 185, 150 (1877)) from allyl iodide, Me<sub>2</sub>CO and Zn. Yavorskii (*C. A.* 9, 1019) obtained better results by using Mg instead of Zn at 0-10° (cf. also Meisenheimer, Caspar, *C. A.* 15, 3978). C. has obtained A as well as allyldimethylmethyl allyl ether (B) by J.'s method. Pure Me<sub>2</sub>CO and allyl chloride were added to Mg covered with Et<sub>2</sub>O with ice cooling so that the Et<sub>2</sub>O just boiled. The Mg compds. in the reaction mixt. were

dissolved in dd. HCl and the Et<sub>2</sub>O soln. was sepd., washed, dried with K<sub>2</sub>CO<sub>3</sub> and fractionated. The 1st fraction, b. 118–20°, was pure A, m. –73°, d<sub>4</sub><sup>17</sup> 0.83553, d<sub>4</sub><sup>17</sup> 0.83452, n<sub>D</sub><sup>17</sup> 1.4300. The 2nd fraction, b. 187–94°, consists of B, a pale mobile oil, b. 190–93°, d<sub>4</sub><sup>17</sup> 0.8765, d<sub>4</sub><sup>17</sup> 0.8754, n<sub>D</sub><sup>17</sup> 1.4750. The presence of 2 double bonds was detd. by the fact that in CCl<sub>4</sub> B absorbed 4.03 atoms Br in 30 mins. When an equiv. amt. of Ac<sub>2</sub>O was added to the reaction mixt. contg. A and B the Mg compds. underwent a change. On treating with H<sub>2</sub>O after 2 hrs. a brown Et<sub>2</sub>O soln. was sepd., which was washed with Na<sub>2</sub>CO<sub>3</sub> soln. On fractionation 2 fractions (1) b<sub>11</sub> 46–8°; (2) b<sub>13</sub> 75–85°, were obtained. (1) is allyldimethylcarbinol acetate, b. 136–8°, d<sub>4</sub><sup>15</sup> 0.88797, d<sub>4</sub><sup>16</sup> 0.88720, n<sub>D</sub><sup>16</sup> 1.4230. (2) is a yellow oil consisting of the ether.

F. J. WITZEMANN

Action of silver sulfate in sulfuric acid solution on ethyl bromide. E. A. SHILOV. *Bull. Inst. Poly. Ivanovo-Voznesensk.* 6, 233(1922).—Alc. is now found (cf. C. A. 17, 1395) among the products of the action of a H<sub>2</sub>SO<sub>4</sub> soln. of Ag sulfate on EtBr, so that the EtHSO<sub>4</sub> formed evidently undergoes considerable hydrolysis. The reaction proceeds quant. in accordance with the equation  $\text{HAgSO}_4 + \text{EtBr} = \text{AgBr} + \text{EtHSO}_4$ .

J. C. S.

Action of dimethyl sulfate and of potassium methyl sulfate upon organic monoacids in the absence of water. L. J. SIMON. *Compt. rend.* 176, 583–6(1923).—Me<sub>2</sub>SO<sub>4</sub> is generally used as a methylating agent in the presence of H<sub>2</sub>O, although Graebe showed that it would act upon the anhyd. salts of org. acids. It can also be used to methylate org. acids by heating with the free acid. Thus, AcOMe is prepd. in 80–100% yield by heating Me<sub>2</sub>SO<sub>4</sub> with AcOH; at 120° the pure ester dists. over, according to the equation:  $\text{AcOH} + \text{Me}_2\text{SO}_4 \longrightarrow \text{MeHSO}_4 + \text{AcOMe}$ . At 200° the reaction  $\text{AcOH} + \text{MeHSO}_4 \longrightarrow \text{Me}_2\text{SO}_4 + \text{AcOMe}$  takes place. In place of Me<sub>2</sub>SO<sub>4</sub>, MeKSO<sub>4</sub> may be used.

T. S. CARSWELL

A graphical interpretation of the separation of a gaseous mixture of mono-, di- and trimethylamines. RUDOLF MICHEL. *Chem.-Ztg.* 47, 173–4(1923).—M. gives a graphical method for detg. the compn. of a gaseous mixt. of mono-, di- and trimethylamines at different temps.

R. CHESTER ROBERTS

Arsenic compounds. HEINRICH WIELAND. *Ann.* 431, 30–40(1923).—The products of the reaction of 2.5 mols. AlCl<sub>3</sub> upon 1 mol. AsCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> contain PhAsCl<sub>2</sub> (A), Ph<sub>2</sub>AsCl (B), Ph<sub>3</sub>As (C) and As. Under the best conditions, 181 g. AsCl<sub>3</sub> gave 30 g. A, 6 g. B and 85 g. C. 11 g. PhNIINII<sub>3</sub> and 26 g. Ph<sub>2</sub>AsO<sub>2</sub>H gave 20 g. C when warmed to 150° for a few min. (With A. BLOEMER.) The action of C<sub>6</sub>H<sub>5</sub> upon AsCl<sub>3</sub> is again described (see Green and Price, C. A. 15, 2063). (CHC:CH)<sub>3</sub>As, b<sub>11</sub> 138°, m. 13°. CHC:CHAsCl<sub>2</sub>, b<sub>13</sub> 77–8°. The corresponding arsonic acid m. 129°. (CHC:CH)<sub>2</sub>AsCl, b<sub>11</sub> 113°. The corresponding arsonic acid m. 122°. (With H. WESCHER.) *Cacodyl carbide*, Me<sub>3</sub>AsC : CAsMe<sub>3</sub>, by the interaction of Me<sub>2</sub>AsCl and (BrMgC : )<sub>2</sub>, golden yellow oil, b<sub>14</sub> 84.5°.

C. J. WEST

The catalytic action of hydrogen ions in the saponification of esters. S. C. J. OLIVIER and G. BERGER. *Rec. trav. chim.* 41, 637–45(1922).—With few exceptions the sapon. of esters is accelerated notably by the action of strong mineral acids. The velocity of sapon. of esters of H<sub>3</sub>PO<sub>4</sub>, sulfonic acids and Me<sub>2</sub>SO<sub>4</sub> and Et<sub>2</sub>SO<sub>4</sub> (Kremann, C. A. 11, 2988; Klemenc and Edhofer, C. A. 12, 2194) is not influenced by the H<sup>+</sup> ion. Recently in a study of the mobility of Cl in substituted benzyl chlorides O. (C. A. 16, 2851) noted that H<sub>2</sub>SO<sub>4</sub> (2.2 g. mols. per l.) did not accelerate the sapon. of these chlorides. This suggests that in general the sapon. of esters of strong acids is not accelerated by H<sup>+</sup> ions. Various esters were examd. in order to verify this supposition. PhCH<sub>2</sub>Cl was first examd. more fully. It was found that acids appreciably influence its hydrolysis. Under the same conditions, i. e., 96 hrs. at 40°, AcOCH<sub>2</sub>Ph without acid was not sapond. but with 0.0244 g. mol. H<sub>2</sub>SO<sub>4</sub> per l. 50% was sapond.



The sapon. of *l*-monochlorohydrin is likewise not affected by the  $H^+$  ion (cf. Senter, *C. A.* 2, 2221). The same is true for BuCl and iso-BuCl. The rule having been established for esters of  $H_3PO_4$ ,  $H_2SO_4$  and HCl, it remained to test  $HNO_3$ . Similar expts. on  $EtONO_2$  showed that the  $H^+$  ion is practically without influence on its sapon. The sapon. of  $EtOAc$  with  $HNO_3$  is much faster than that of  $EtONO_2$ , which supports Ostwald's view that the acid acting as catalyst does not form its own ester as an intermediate step. Are the strong acids interchangeable or is there a specific effect requiring the acid, the ester of which is being used?  $CCl_3CO_2Me$  was hydrolyzed alone and with 0.05 g. mol. HCl per l. The  $H^+$  ions showed a weak positive effect. Since  $CCl_3CO_2H$  approaches the strong mineral acids in its properties this result conforms with the others. The results of Sudborough (*C. A.* 7, 324) in the sapon. of esters of propionic, levulinic and pyruvic acid showed that HCl accelerates them 900, 170 and 12 times, resp. Since pyruvic acid is a strong acid these results also conform. Other data of the same kind are cited from the literature. O. and B. have not examd. the inverse reaction, i. e., esterification, but a similar rule seems to exist. Sirks (*C. A.* 2, 2639) found that in the presence of HCl org. acids having a dissociation const. of more than 1 are esterified more slowly than the weaker acids. In esterification without catalysts a greater velocity is observed for the stronger acids (Sudborough, *C. A.* 7, 324) from which one can deduce that the sapon. of these strong acids is less influenced by the addn. of HCl. The older theories of the mechanism of sapon. do not accord well with the above facts but the theory of Stieglitz (*C. A.* 2, 996, 1687; 7, 3961) involving the formation of

oxonium salts is satisfactory. It cannot be decided whether it is the ion  $R'CO \begin{smallmatrix} R \\ \diagup \\ H \end{smallmatrix}$  that

reacts in sapon. in acid soln. (Stieglitz) or whether the ester at the moment of transformation into an oxonium salt is activated and hydrolyzes more easily (in the sense of the theory of Böseken and Prius).

F. J. WITZEMANN

**Preparation of esters and glycidates of alkylglycerols.** RAYMOND DELABY. *Compt. rend.* 176, 539-91 (1923).—The dibromohydrins were prepd. from the vinylalkylcarbinols (*C. A.* 17, 537) by the addn. of 1 mol. of Br. *1,2-Dibromo-3-butanol*  $b_{11}$  102-5°,  $d_4^{20}$  1.976,  $d_4^{20}$  1.944,  $n_D^{23}$  1.5405. *1,2-Dibromo-3-pentanol*  $b_{11}$  112-5°,  $d_4^{20}$  1.855,  $d_4^{20}$  1.828,  $n_D^{20}$  1.5327. *1,2-Dibromo-3-hexanol*  $b_{11}$  126-9°,  $d_4^{20}$  1.751,  $d_4^{20}$  1.724,  $n_D^{23}$  1.5230. *1,2-Dibromo-3-heptanol*  $b_{11}$  132-3°,  $d_4^{20}$  1.638,  $d_4^{20}$  1.613,  $n_D^{26}$  1.5191. The tribromohydrins were prepd. by the action of  $PBr_3$  upon the dibromohydrins. *1,2,3-Tribromobutane*  $b_{11}$  110-3°,  $d_4^{20}$  2.2118,  $d_4^{20}$  2.190,  $n_D^{26}$  1.5691. *1,2,3-Tribromopentane*  $b_{11}$  125-8°,  $d_4^{20}$  2.116,  $d_4^{20}$  2.095,  $n_D^{26}$  1.5621. *1,2,3-Tribromohexane*  $b_{11}$  137-41°,  $d_4^{20}$  1.914,  $d_4^{20}$  1.896,  $n_D^{26}$  1.5451. *1,2,3-Tribromoheptane*  $b_{11}$  148-9°,  $d_4^{20}$  1.850,  $d_4^{20}$  1.827,  $n_D^{26}$  1.5394. The epibromohydrins were prepd. by the action of finely divided KOH upon the dibromohydrins in  $Bt_2O$ . *Methylglycerol epibromohydrin*  $b.$  142-4°,  $d_4^{20}$  1.493,  $d_4^{20}$  1.468,  $n_D^{26}$  1.4685. *Butylglycerol epibromohydrin*  $b_{11}$  202-5°,  $b_{11}$  91°,  $d_4^{20}$  1.246,  $n_D^{26}$  1.4675. *Methylglycerol tribenzoate*  $m.$  79-80° (recrystd. 95°). *Ethylglycerol tribenzoate*  $m.$  99-100°. T. S. CARSWELL.

**Cyclic condensation products of acetone with 1,3-diols.** J. BÖRSEKEN WITH G. SCHAEFFER AND P. HERMANS. *Rec. trav. chim.* 41, 722-3 (1922).—The report of Mannich and Brose (*C. A.* 17, 728) on a cyclic compd. of euneheptitol with  $Me_2CO$  caused B. *et al.* to report on analogous compds. v. Loon (*Thesis, Delft* 1919, p. 59-60) obtained cyclic  $Me_2CO$  derivs. of poly-HO compds. in which he suspected the ring to be 6-atomic. Later Schaefer dissolved 35 g. powdered  $C(CH_2OH)_4$  in 668 cc.  $Me_2CO$  (1% HCl). After 2 days at room temp. the HCl was neutralized with powdered KOH, the  $Me_2CO$  distd. off and the product extd. with cold  $C_6H_6$ . On evapn. the *diacetonated deriv.* of *pentaerythritol*,  $Me_2C(OCH_2)_2C(CH_2O)_2CMe_2$ ,  $m.$  116°, sep'd. The residue crystd. from boiling  $C_6H_6$  gave the *monoacetone deriv.*  $Me_2C(OCH_2)_2C(CH_2OH)_2$ ,  $m.$  135°. The product of condensation of  $C(CH_2OH)_4$  with 2 mols. *d*-3-methylcyclohexanone

as well as *monoacetic* derivs. of  $O_2NC(CH_2OH)_2$ ,  $O_2NMeC(CH_2OH)_2$ ,  $Br_2C(CH_2OH)_2$  were also obtained and will be described later. Hermans (see also C. A. 15, 3630) has now obtained *acetone-propane-1,3-diol*.

E. J. WITZEMANN

**Derivatives of aminoaldehydes.** ERICH RADDE. *Ber.* 55B, 3174-9 (1922).—It was attempted to prep. the  $NH_2$  aldehydes by the reduction of the  $NH_2$  acids, protecting the  $NH_2$  group by the phthalyl group which was to be later hydrolyzed off. Of a no. of methods tried the reduction of the  $CO_2H$  by  $H_2$  in the presence of Pd was the only one to give the phthalimido aldehydes. Even this method (cf. Rosenmund, *Ber.* 51, 585) was only applicable to the  $\alpha$ -phthalimido acid chlorides and not to the  $\beta$ -,  $\gamma$ -, and  $\delta$ -comps. *Phthalimidopropionaldehyde*, m.  $111^\circ$  (*semicarbazone*, m.  $228.5^\circ$ ), and *phthalimidoacetaldehyde*, m.  $114.5^\circ$  (*phenylhydrazone*, m.  $163-5^\circ$ ; *oxime*, m.  $166-8^\circ$ ), were prepd. It was found that the action of NaOMe on *phthalylglycyl nitrile* gave  $HCO_2C_6H_4CONHCH_2CN$ . *Phthalyl- $\alpha$ -alanil nitrile* acted similarly. O. B. H.

**Pyruvic acid from lactic acid.** J. G. SMULL AND P. SIBKOW. *Chem. Mel. Eng.* 28, 357-8 (1923).—The electrolytic oxidation of lactic acid, with Pt electrodes, in a cell in which the anode and cathode compartments were sepd. by a porous cup and so arranged that the anode compartment could be stirred gave the following results. With an anolyte consisting of 27% lactic acid and 20%  $H_2SO_4$  and a catholyte of 20%  $H_2SO_4$  the products were AcOH and  $CO_2$ ; with an anolyte of Cu lactate (6 parts in 100 cc.) and enough  $Cu(NO_3)_2$  to raise the Cu concn. to 20% and a catholyte of 20% Cu as  $Cu(NO_3)_2$  the products were AcH, AcOH,  $HCO_2H$ ,  $CO_2$  and a ppt. of Cu pyruvate; with an anolyte of 40% Na lactate contg. 4.8% NaOH and a catholyte of 8% NaOH the products were mainly AcH,  $HCO_2H$  and  $CO_2$ . When a perforated Pb anode in 27% Na lactate made alk. with NaOH and an Fe wire gauze cathode in 6% NaOH were used, pyruvic acid was obtained from an insol. substance which was formed, probably a basic Pb salt of the acid. G. W. STRATTON

***d*-Malic acid and the utilization of ammonium molybdomalate for the resolution of *dl*-malic acid.** F. DARMOIS AND J. PERIN. *Compt. rend.* 176, 391-4 (1923); cf. C. A. 15, 2831. —Since the *dl*- $NH_4$  dimolybdate does not deposit from its solns., *dl*-malic acid can be very simply sepd. into its 2 active constituents. The high rotatory power of the molybdic comps. is an excellent criterion of the purity of the substances obtained. D. MACRAE

**Action of acetic anhydride upon uric acid.** HEINRICH BILTZ AND WALTER SCHMIDT. *Ann.* 431, 70-104 (1923); cf. Ger. patents 121,224 (1901); 126,797 (1901).—The action of  $Ac_2O$  upon uric acid in the presence of  $C_3H_5N$  gives *g-acetyl-2,6,8-triketo-8-methyl-8-dihydropurine (A)* and not 2,4-diketo-5,6-[diacetylamino]pyrimidine as earlier supposed. In boiling  $H_2O$  the soly. is about 1.8, the soln. being yellow even with the purest prep. The above formula is confirmed by the fact that only 1 Ac is split off by NaOH or HI the resulting product being *2,6,8-trioxy-8-methyl-3,9-dihydropurine (B)*, whose soly. in boiling  $H_2O$  is 1.8, but the resulting soln. is colorless. *K salt*, decomp.  $415-7^\circ$ ; *Ag salt*, amorphous, decompd. by light. *Perchlorate*,  $C_8H_5O_8N_4 \cdot 2HClO_4$ , turns red at  $80^\circ$ , decomp.,  $163-4^\circ$ ;  $H_2O$  decomp. it into its components. *Sulfate*, gradually carbonizes on heating;  $H_2O$  quickly decomp. it into the components; *hydrochloride*, *nitrate*, likewise easily decompd. by  $H_2O$ . *B* apparently reacts with  $HCHO$  in alk. soln., but no cryst. product could be isolated. The usual oxidizing agents, acting upon *B*, lead to no definite products; either the action was very slight or too vigorous decomposition occurred. Cl and an aq. suspension of *B* gave alloxan. Long heating of *A* or *B* with  $Ac_2O$  split off the 9-OH group, giving 8-methylxanthine (*C*). *B benzoate*, which turns brown about  $300^\circ$  and carbonizes without decompn. at  $420^\circ$ , resulted by shaking the K salt of *B* with  $BzCl$  in  $CCl_4$ . The reduction of *B* with  $HI$  on the  $H_2O$  bath for 3 hrs. gave *8-methyl-9,10-dihydroxanthine*, also formed in the sapon. of *A* with

HI, which does not m. or decomp. at 450°. Oxidation gives alloxan. *Hydroiodide*, decomp. about 200°.  $\text{Me}_2\text{SO}_4$  reacts with *B* to give the 3,8-dimethyl deriv., decomp. 305-6°. Since HI does not split off Me, both Me groups must be attached to N. Oxidation with Cl gave methylalloxan. A further proof of the position of the Me groups is that  $\text{Ac}_2\text{O}$  gives 3,8-dimethylxanthine. Detailed directions are given for the prepn. of 2,4-diketo-5,6-diaminopyrimidine and the Na salt, the hydrochloride and nitrate. The action of  $\text{Ac}_2\text{O}$  upon the Na salt gave a diacetate of *B*. If the Na salt contains  $\text{Na}_2\text{CO}_3$ , there is formed a Na salt with 1  $\text{H}_2\text{O}$ ,  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{N}_4\text{Na} \cdot \text{H}_2\text{O}$ , sinters 135°, decomp. 258-60°, and readily changes into the diacetate by heating 1 min. with 10% NaOH. Directions are given for the purification of *C*. Oxidation in alk. soln. gave only  $(\text{CO}_2\text{H})_2$ , while in acid soln. alloxan is also formed. *Perchlorate*, decomp. 292-4°; *hydroiodide*, decomp. with evolution of I at about 200°; *sulfate*, nitrate and *dimnitrate*, all gradually carbonize without decompn. C. J. WESS

Optical rotatory power of sugars in hydrochloric acid. L. ZECHMEISTER. *Z. physik. Chem.* 103, 316-36(1922).—Aldohexoses and aldopentoses in cold, fuming HCl suffer a measurable reversible transformation, which is indicated by a marked increase in the  $[\alpha]_D$  values to a const. final value. The magnitude of this final value increases with the HCl concn. In HCl of high concn. the abs. value of  $[\alpha]_D$  exceeds the rotatory power of the  $\alpha$ -form in pure  $\text{H}_2\text{O}$ . For *D*-glucose in 46.7% HCl,  $[\alpha]_D^{+12} = +202$ . H. JERMAIN CREIGHTON

The action of ozone on solutions of pure maltose. C. W. SCHONEBAUM. *Rec. trav. chim.* 41, 501-2(1922).—These expts. were done as those on other sugars (*C. A.* 16, 1215, 3072). 5% maltose (*A*) solns. were ozonized 3 hrs. and the solns. analyzed polariscopically and titrimetrically. In neutral soln. *A* was not decompd. at room temp. nor at 70°. In 0.1 *N* acid soln. it was not decompd. at room temp. but rapidly inverted at 70°. In 0.1 *N* alk. soln. *A* was 35% decompd. at room temp. E. J. W.

The action of hydrogen peroxide on pure solutions of glucose, fructose, sucrose lactose and maltose. C. W. SCHONEBAUM. *Rec. trav. chim.* 41, 503-8(1922).—The purpose of these expts. was to det. under what conditions these sugars are not acted upon by  $\text{H}_2\text{O}_2$  so that  $\text{H}_2\text{O}_2$  may be used to improve their solns. 4 g. of the sugar in 80 cc. of  $\text{H}_2\text{O}$ , 0.1 *N*  $\text{H}_2\text{SO}_4$  or 0.1 *N* NaOH + 4 cc. 3%  $\text{H}_2\text{O}_2$  were made up to 100 cc. and kept 3 hrs. at room temp. or 70°. The results are summarized in the table.

	Neutral soln.		0.1 <i>N</i> acid soln.		0.1 <i>N</i> alk. soln.	
	Room temp.	70°.	Room temp.	70°.	Room temp.	70°.
glucose	no decompn.	trace decompn.	no decompn.	trace decompn.	trace decompn.	
fructose	no decompn.	trace decompn.	no decompn.	trace decompn.	trace decompn.	
sucrose	no decompn.	10% inverted	inverted <sup>1</sup>		no decompn.	
lactose	no decompn.	no decompn.	no decompn.	trace decompn.	trace decompn.	
maltose	no decompn.	trace decompn.	no decompn.	inversion & decompn.	trace decompn.	

<sup>1</sup> Inversion is not influenced by  $\text{H}_2\text{O}_2$ .

These results are only applicable at the great  $\text{H}_2\text{O}_2$  diln. used. At higher concns. the sugars are decompd. more rapidly. At low  $\text{H}_2\text{O}_2$  concns. the attack on the sugars (except sucrose) is insignificant even at 70°. In practice the nonsugar content of the solns. protects the sugars. Special expts. showed that heating neutral solns. of sucrose in the presence of even less than 0.15%  $\text{H}_2\text{O}_2$  gave considerable inversion. The pres-

ence of minimal alkalinity protects sucrose from  $H_2O_2$ . Sugar juices can be treated with  $H_2O_2$  if the soln. is kept alk. E. J. WITZEMANN

**Stereoisomerism of cyclic alcohols, aldehydes and carboxylic acids.** A. SKITA, H. HAUBER AND R. SCHÖNFELDER. *Ann.* **431**, 1–30 (1923).—The hydrogenation of the 3 cresols with colloidal Pt at  $70^\circ$  in acid soln. (HCl, AcOH) gives the 3 *cis*-methylcyclohexanols, while if the operation is carried out in a cold neutral soln. the *trans*-derivs. result. In a slightly acid soln. mixts. of the 2 result. *2'-Hydroxy-1'-methylcyclohexane*, b.  $165-6.5^\circ$ , results in 80% yield by the hydrogenation of *o*- $HOC_6H_4Me$  with colloidal Pt soln. at  $70-80^\circ$ . *Semicarbazone*, m.  $191^\circ$ . *2'-Hydroxy-1'-methylcyclohexane*, b.  $169.5-70.5^\circ$ , results in 75% yield upon hydrogenation of 1-methylcyclohexane-2-one in AcOH. *Phenylurethan*, m.  $95^\circ$ . Reduction of *o*- $HOC_6H_4Me$  gave a 76% yield of the same compd. The *2'-iodo deriv.* b.  $96^\circ$ ; the Grignard reagent from this, treated with  $CO_2$ , gives *1'-methylcyclohexane-2'-carboxylic acid*, b.  $238.5-40^\circ$ ; *amide*, m.  $152-3^\circ$ ; *anilide*, m.  $106^\circ$ . The acid was obtained in 83% yield by the reduction of *o*- $MeC_6H_4CO_2H$  in acid soln. *Methyl ester*, b.  $191.5-2^\circ$ ,  $d_4^{20}$  0.970,  $n_D^{20}$  1.4476. Reduction of the Et ester with Na in EtOH gives *1'-methylcyclohexane-2'-carbinol*, b.  $188-9^\circ$ ,  $d_4^{20}$  0.9342,  $n_D^{20}$  1.4721. The benzoate is an oil. Upon oxidation, the carbinol yields the *aldehyde*, b.  $70^\circ$ ; *semicarbazone*, m.  $137-8^\circ$ . *2'-Hydroxy-1'-methylcyclohexane* is obtained in 81% yield from the ketone by reduction with Na in moist  $Et_2O$  or in 80% yield by reduction of the ketone or *o*- $HOC_6H_4Me$  in neutral soln. with Pt. It b.  $166.2-6.7^\circ$ , and forms a phenylhydrazone, m.  $105^\circ$ . *1'-Methylcyclohexane-2'-carboxylic acid*, obtained through the Grignard reaction as above or by heating the isomeric acid with HCl, b.  $241-2^\circ$ , m.  $52^\circ$ . *Amide*, m.  $180^\circ$ ; *anilide*, m.  $152^\circ$ . *Methyl ester*, b.  $191-2^\circ$ ,  $d_4^{20}$  0.957,  $n_D^{20}$  1.4440. The corresponding *carbinol* b.  $192-2.5^\circ$ ,  $d_4^{20}$  0.9224,  $n_D^{20}$  1.4665; the *aldehyde*, b.  $72^\circ$ ,  $d_4^{20}$  0.912,  $n_D^{20}$  1.4498. The *semicarbazone* m.  $152^\circ$ . *1'-Methylcyclohexane-4'-carboxylic acid*, b.  $198-8.5^\circ$ , was prepd. by hydrogenation of *p*- $MeC_6H_4CONH_2$  and sapon. of the resulting product. *4'-Hydroxy-1'-methylcyclohexane*, b.  $173.5-3.8^\circ$ ; *phenylurethan*, m.  $98^\circ$ . *4'-Hydroxy-1'-methylcyclohexane*, b.  $172.7-3.1^\circ$ ; *phenylurethan*, m.  $124-5^\circ$ . Both alics. yielded the same acid, m.  $52^\circ$ . *1'-Methylcyclohexane-4'-carbinol*, in 38% yield, b.  $197.5-8.5^\circ$ . *Aldehyde*, b.  $75-6^\circ$ ; *semicarbazone*, m.  $183^\circ$ . *3'-Hydroxy-1'-methylcyclohexane* b.  $174.6-5^\circ$ ; *phenylurethan*, m.  $91^\circ$ . The corresponding *1'-deriv.* b.  $171.5-2.5^\circ$ , and gave a *phenylurethan*, m.  $76^\circ$ . *1-Methylcyclohexane-3-carbinol*, b.  $198-9^\circ$ ,  $d_4^{20}$  0.9222;  $n_D^{20}$  1.4641; the corresponding *aldehyde*, b.  $95^\circ$ ,  $d_4^{20}$  0.9086,  $n_D^{20}$  1.4447; *semicarbazone*, m.  $157.5^\circ$ . Fractionation of a mixt. of naphthenic acids from Caucasian petroleum (Balachany) gave a fraction  $C_8H_{16}O_2$ , b.  $235-40^\circ$ ,  $d_4^{20}$  0.963,  $n_D^{20}$  1.4481; *methyl ester*, b.  $190-2^\circ$ ,  $d_4^{20}$  0.926,  $n_D^{20}$  1.4328. The *amide* m.  $126^\circ$ . Comparison with the synthetic acid shows that they are not identical and the assumption is made that it contains a 5-membered ring. C. J. WESER

**The occurrence of *d*-quercitol in the seeds of *Achras sapota*.** L. A. W. VAN DER HAAR. *Rec. trav. chim.* **41**, 784–6 (1922).—Quercitol or cyclohexane-1,2,3,4,5-pentol occurs in isolated instances in the *d*- and *l*-form in plants. v. d. H. found in seeds of *A. sapota*, *L.* considerable amts. of *d*-quercitol (*A*) identical with that from acorns. 3 kg. of the dry seed flour that had been freed from fat with petroleum ether was extd. cold with 99% MeOH. The MeOH soln. was concd. and mixed with several vols.  $Et_2O$ , which seps. a thick sirup, contg. saponin which soon crystals. After a few days the sirup was treated with MeOH, which dissolved the saponin almost completely, leaving 140 g. sweet crystals composed mostly of sucrose and saponin and a small amt. of *A*. 10-g. portions were extd. with 99% MeOH and then not too long with 70% EtOH to dissolve most of the sucrose and some *A*. The remaining crystals were recrystn. from 70% EtOH, which gave 19 g. faintly sweet crystals. Recrystn. was continued until the crystals showed no reduction with Fehling soln. after heating with 5% HCl.

The *A* obtained m. 233–4°,  $\alpha_D^{15}$  24.37°, with  $\text{HNO}_3$  gave mucic acid m. 214°, and gives the Lieben iodoform reaction. The data given in some of the handbooks for the m. p. of *A* are wrong. The substance obtained by Bouchardat (*J. pharm. chim.* [4] 14, 347 (1871)) from *A. sapota* and called lactose is no doubt a mixt. of sucrose and *A*.

R. J. WITZEMANN

Can Kekulé's benzene theory still be considered satisfactory? C. W. A. LELY. *Chem. Weekblad* 19, 593–9(1922); 20, 90–6(1923).—L.'s theory, which is supposed to

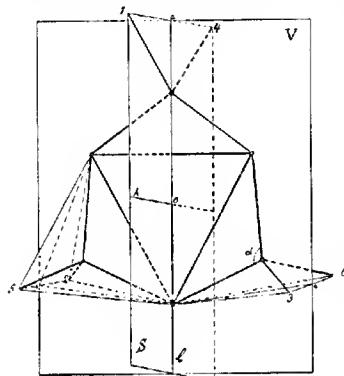


Fig. 1

disubstituents observed. To satisfy the last two requirements a special hypothesis is necessary, *vis.*: the hypothesis of *synchronous rotation* of the 3 pairs of H atoms attached to the secondary C atoms. If this holds and if we consider that in Fig. 1, the whole formula is sym. as regards the plane *AO* and also the plane *V* we may conclude that the following substituents are equiv.: 1,2 = 4,5 = 5,6 = 2,3 = 3,4 = 1,6 (*o*); 1,3 = 1,5 = 3,5 = 2,6 = 2,4 = 4,6 (*m*); 1,4 = 2,5 = 3,6 (*p*). This includes all possible combinations.

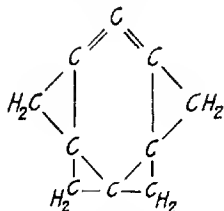


Fig. 2

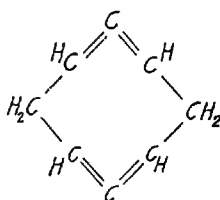


Fig. 3

A similar proof is possible for tri- and tetra-substituted compds. Optical asymmetry is also impossible owing to the sym. rotation. The formula also allows an explanation of the special chem. properties of compds. with 2 or more substituents: *e. g.*, *m*-substituents are always on the same side of the plane of the C atoms, and therefore, in sym.- $\text{C}_6\text{H}_3(\text{NO}_2)_3$  the three  $\text{NO}_2$  groups have a strong attracting force on other mols. *p*-Substituents are on the same C atom; for this reason quinone is formed by oxidizing  $\text{PhNH}_2$ , or *p*-toluidine is formed from  $\text{PhNHMe}$ . L. can explain on the basis of his new theory

a no. of similar phenomena described by Holleman in his book: "Die direkte Einführung von Substituenten in den Benzolkern." L., also, introduces new structural formulas for polynuclear compds., e. g., for *naphthalene* (Fig. 2). The typical chem. properties of *cyclooctatetraene*, as described by Willstätter, are best explained by the structural formula in Fig. 3 according to L., while on the basis of the old theory no satisfactory formula can be given as stated by Kroschelt in "Handwörterbuch der Naturwissenschaften," V, 572. An analogous formula is introduced for *pyridine* as illustrated by Fig. 4. The N atom is connected with one H atom according to this theory while in the old theory it is not. Triangle structural formulas are also given for *pyrrole* and *thiophene*. The close chem. relationship of all these compds. with  $C_6H_6$  is manifested by the primary triangle of three C atoms common to all compds. while N or S atoms only replace secondary C atoms. The azines, however, are assumed to have a primary triangle not of C atoms, but of one C atom and two N atoms. The hypothesis of the synchronic rotations is further applied to the trimethylene compds. This hypothesis is, also, better capable of explaining all the isomerism phenomena of maleic and of fumaric acids and their derivs. than the theory of van't Hoff.

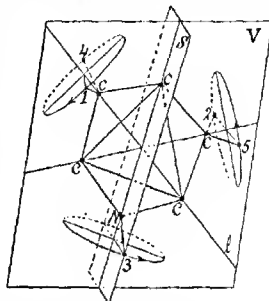


Fig. 4

**The benzene formula according to Lely.** S. C. J. OLIVIER. *Chem. Weekblad* 20, 27-8 (1923).—Criticism of Lely's hypothesis of "synchronic rotations," and his explanations of the chem. properties of substituted benzenes on the basis of his formula, (e. g., the formation of *p*-quinone from  $PbNH_2$ ).

R. BEUTNER

R. BEUTNER

**What requirements must be satisfied by a benzene formula?** H. J. PRINS. *Chem. Weekblad* 20, 28-9 (1923).—Lely's benzene formula is unsatisfactory (1) because its "triangle" C atoms should take up H readily; (2) because the H atom standing next to  $-CO_2H$  in  $BzOH$  should be readily replaced by Cl, resulting in the formation of *p*- $ClC_6H_4CO_2H$  (as a matter of fact, however, the *m*-compd. is formed); (3) because hydroquinol having the group  $\begin{array}{c} \diagup \\ C \\ \diagdown \end{array} \begin{array}{c} OH \\ OH \end{array}$  should be quite unstable; (4) because terephthalic acid should readily form an anhydride.

R. BEUTNER

**The structural formula of benzene.** H. A. J. SCHOUTISSEN. *Chem. Weekblad* 20, 29-31 (1923).—These criticisms of Lely's theory contain the same arguments as the two preceding ones; besides it is pointed out that in the "primary C triangle" an immense tension of the valencies should exist, and that this arrangement cannot be stable, therefore. It is, also, pointed out that the Kekulé theory is supported by the modern conceptions of the Lewis-Frazer theory (compare Fraser, *C. A.* 16, 1218).

R. BEUTNER

✓ **A reply concerning the benzene theory.** C. W. A. LELY. *Chem. Weekblad* 20, 82-3 (1923).—L. defends his hypothesis of synchronic rotation and other details of his theory against the criticisms of Olivier, Prins and Schoutissen. According to his view the synchronic rotation keeps apart the substituent groups in the *p*-compds., e. g., in hydroquinol.

R. BEUTNER

**Once more the benzene formula according to Lely.** S. C. J. OLIVIER. *Chem. Weekblad* 20, 143-4 (1923).—O. maintains the objections raised previously against Lely's theory.

R. BEUTNER

Lely's benzene theory and the so-called aliphatic-aromatic transitions. I. D. VAN ROON. *Chem. Weekblad* 20, 144(1923).—According to Lely's theory, we should expect that aromatic compds. can be formed from trimethylene compds.; no examples of this are known, however. *p*-Substituted cyclic compds. should be formed from aliphatic compds. which have both substituents on the same C atom; this also is not the case. Nor can the formation of ketenes from quinone be observed, which should be expected. Lely's formula would make impossible a triozonide of benzene.

R. BRUTNER

Are the triangle formulas of Lely tenable? H. A. J. SCHOUTISSEN. *Chem. Weekblad* 20, 145(1923).—S. maintains his previous objections against Lely's formula.

R. BRUTNER

Lely's benzene theory. II. G. DERYX AND P. H. HERMANS. *Chem. Weekblad* 20, 145-6(1923).—The authors object to Lely's explanations of fumaric and maleic acids and his criticisms of van't Hoff's theory. Lely's errors are due to the fact that he studied a textbook of organic chemistry published in 1891.

R. BRUTNER

The influence of some substituents in the benzene ring on the mobility of chlorine of the side chain in its relation to the problem of substitution in the benzene ring. S. C. J. OLIVIER. *Rec. trav. chim.* 41, 646-51(1922).—In a preceding paper (*Ibid* 41, 301(1922); cf. *C. A.* 16, 2851) O. studied the influence of Me, Cl, and NO<sub>2</sub> present in the C<sub>6</sub>H<sub>5</sub> ring on the mobility of Cl in the side chain by allowing H<sub>2</sub>O to act upon substituted benzyl chlorides in EtOH. Lately Br has been included in the study. The results now obtained are summarized thus: for *p*-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl  $K_{53} = 164$ ,  $K_{10} = 1.04$ ; *o*-isomer 75, 0.55; *m*-isomer 21.6, 0.144; PhCH<sub>2</sub>Cl 15.5, 0.111; *p*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 9.6, 0.052; *p*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 7.8, 0.0457; *o*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 5.5, —; *o*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 4.44, 0.0236; *m*-ClC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 3.68, 0.0152; *m*-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 3.34, 0.0147; *m*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl 1.40, 0.0063; *o*-isomer 1.30, 0.0052; *p*-isomer 1.15, 0.00491, resp. The results for Br conform with the results obtained for the other substituents. Br is, however, a little more negative than Cl which is the reverse of what was found in the Friedel and Crafts reaction (*C. A.* 8, 3013; 9, 442); cf. also Wibaut *C. A.* 10, 184, and Böeseken, *et al.*, *C. A.* 15, 1023. In the preceding paper (*l. c.*) O. found that the influence of the position of the substituent is less pronounced as the influence of the substituent becomes weaker. This is also true of Br. The ratio of the velocity consts. ( $K_{para}:K_{meta}$ ) diminishes regularly as the substituent becomes more negative. O. intends to exam. a group more negative than NO<sub>2</sub> to see if this ratio continues to diminish. In order to obtain a clearer view of the influence of temp. on the relative velocity of sapon. of the various compds. the consts. were recalcd., putting that of PhCH<sub>2</sub>Cl as 1 at both temps. used. The results show that at the higher temp. the velocity consts. except those of tolyl chlorides approach more closely that of PhCH<sub>2</sub>Cl. The retarding influence of the negative substituents is less pronounced at the higher temp. The order *p*-Me>*o*-Me>*m*-Me>H>*p*-Cl>*p*-Br>*o*-Cl>*o*-Br>*m*-Cl>*m*-Br>*m*-NO<sub>2</sub>>*o*-NO<sub>2</sub>>*p*-NO<sub>2</sub>, however, remains intact for the range 30-83°, and within it the parallelism of the influence of the nature and of the position of the substituent present in the C<sub>6</sub>H<sub>5</sub> ring on the reactivity of Cl of the side chain and on the mobility of the H of the ring.

E. J. WITZEMAN

Phenylnitroacetamide and some of its derivatives. A. J. VAN PESKE. *Rec. trav. chim.* 41, 687-700(1922).—Some time ago v. P. showed (*C. A.* 3, 2692) that PhC(NO<sub>2</sub>ONa)CN (*A*) is sapon. to the corresponding amide by H<sub>2</sub>O<sub>2</sub>. The product, PhCH(NO<sub>2</sub>)CONH<sub>2</sub> (*B*), was isolated as PhCBr(NO<sub>2</sub>)CONH<sub>2</sub> (*C*) on treating the impure oily *B* with Br<sub>2</sub>. The crude product has now been found to be mostly *A*. The sapon. is quant., however, if 30% H<sub>2</sub>O<sub>2</sub> and concd. NaOH are used. The Na salt of *B* then slowly seps., and when filtered off with suction and washed with EtOH is obtained pure (except

for NaOH). This salt in  $H_2O$  gives *C* with  $Br_2$  without forming any oil. The pseudo acid *B* can now be obtained easily and kept several weeks. On adding dil.  $H_2SO_4$  to the Na salt in  $H_2O$  a white ppt. of *B* is formed; this is removed and dried rapidly. When crystd. from  $C_6H_6$  or  $CHCl_3$  *B* gives white needles, m. 82.5–83°. Heating 1.5 hrs. in the  $H_2O$  bath decomp. *B* completely, giving much volatile material including  $N_2$  and  $N_2O$  as well as  $BzCO_2H$ ,  $BzCONH_2$  (*D*),  $PhCN$ ,  $H_2O$  and 2 unidentified deriva. of *D*. About the same decompn. occurs at room temp. in several months. The Na salt of *B* with  $Cl_2$  gives phenylchloronitroacetamide (*E*), m. 107–15°. The *I* deriv. cannot be obtained in this way since phenyliodonitroacetamide (*F*) reacts with NaI, giving *A*. *A* in  $H_2O$  treated with  $HNO_3$  to a slight turbidity and then with concd.  $AgNO_3$  soln. sepd. the  $Ag$  salt of *B* which, treated in  $Et_2O$  suspension with dry  $I_2$  gave a soln. from which *F* sepd. as yellow rods. Both *C* and *E* react like *F* with KI, liberating *I* quant. *C*, *E* and *F* all behave alike on heating above 115°;  $NO$  and halogen are evolved and the mass explodes presently. In the brown oil remaining from  $E$   $H_2O$ ,  $BzCN$ ,  $BzCl$ ,  $BzOH$ ,  $BzCO_2H$ ,  $PhCCl_2CONH_2$  and an unknown compd., m. 113–4.5°, were found. *C* gave  $BzCN$ ,  $BzOH$ ,  $H_2O$ ,  $BzCO_2H$ ,  $BzCONH_2$  and probably  $PhCHBr$ . The behavior of *C*, *E* and *F* is thus analogous to that of other compds. contg. the group  $:C(NO_2)Br$  (*Cl* or *I*), such as  $O_2NCBr(CO_2Et)_2$  (Willstätter, Hottenroth, *Ber.* 37, 1775 (1904)),  $PhCBr(NO_2)CN$  (Flürschheim, *J. prakt. Chem.* [2] 66, 321 (1902)) and bromonitrofluorene (Wislicenus, Waldmüller, *C. A.* 3, 174). Only the formation of  $BzCl$  from *E* is distinctive. The splitting off of  $CN$  might be taken to support the formula for true  $NO_2$  compds.,  $R'R''C(NO_2)X$ , proposed by Hantzsch and Voigt (*C. A.* 6, 997) on the basis of absorption spectra. *C*, *E* and *F* are easily sol. in alkali hydroxides and are deeply attacked. On acidifying the soln. of *E* phenylchloronitromethane was obtained as an oil. The  $NH_2$  group was sapon. and  $CO_2$  evolved. The result was the same with *C*. With *F* the result is different;  $BzCN$  is evolved. Wislicenus and Fischer (*C. A.* 4, 2931–2) sapon.  $o$ - $BrC_6H_4C(:NO_2Na)CN$  with 3%  $H_2O_2$  and had the same troubles that v. P. had previously encountered with *A*. After perfecting his method for *A* v. P. treated  $o$ - and  $p$ - $BrC_6H_4C(:NO_2K)CN$ . The corresponding amides and free pseudoacids of these compds., which are more stable than *B* itself, are now all readily obtainable. In some preliminary expts.  $Et$  hydroperoxide and  $PhCH_2CN$  were stirred for a long time with the addn. of  $KOH$ . A colorless well crystd. compd. that appears to be  $PhCH_2C(:NH)O_2Et$  was obtained. It is not now claimed that similar compds. are always obtained in the sapon. with  $H_2O_2$ . E. J. W.

The preparation and separation of *o*- and *p*-chloroaniline. H. C. BASHIOM AND P. O. POWERS. *Ind. Eng. Chem.* 15, 407–8 (1923).—*p*-Chloroaniline was prepd. by the reduction of  $p$ - $ClC_6H_4NO_2$  with  $Fe$  and  $Cl$ , followed by neutralization of the acid and steam distn. of the base. A mixt. of *p*- and *o*- $ClC_6H_4NO_2$  was reduced, and the reduction mixt. was steam distd. after the addn. of nearly 1 equiv. of acid, when the  $o$ - $ClC_6H_4NH_2$  only distd. over. T. S. CARSWELL

Action of the oxides and the oxy acids of nitrogen on diphenylurethan. HUGH RYAN AND ANNE DONNELLAN. *Sci. Proc. Roy. Dublin Soc.* 17, 113–8 (1923).— $Ph_2NCO_2Et$  (*A*) allowed to stand 5 days with concd.  $HNO_3$  gave the 4-nitro deriv. (*B*). Fuming  $HNO_3$  yielded the 4,4'-( $NO_2$ )<sub>2</sub> deriv. (*C*), prisms, m. 68°. Heated 5–6 hrs. with 1.5 parts concd.  $HNO_3$  and 3 parts concd.  $H_2SO_4$ , the product was the 2,4,4',4'-tetranitro deriv. (*D*), m. 184–5°. In dil. soln., *A* was allowed to stand with  $HNO_3$  in  $AcOH$  or  $CCl_4$  during 4–5 weeks; in the latter case, besides *B*, the 2,4'-( $NO_2$ )<sub>2</sub> deriv. (identified only through hydrolysis products) was formed. *D* was also made by nitrating *B*. *A*, in  $CCl_4$  with  $NO_2$ , gave, after some weeks, *C*, and some *E*. Attempts to prep. *B*, *C*, *D*, or *E* by heating the corresponding amine under pressure for some hours with  $ClCO_2Et$  at 160–80° were unsuccessful in each case. B. H. NICOLET



**Action of the oxides and the oxy acids of nitrogen on ethyl-*o*-tolylurethan.** HUGH RYAN and NICHOLAS CULLINANÉ. *Sci. Proc. Roy. Dublin Soc.* 17, 119-24(1923).—*Ethyl-*o*-tolylurethan*,  $C_8H_7NEtCO_2Et$  (A), oily liquid, b.  $255^\circ$ , lost its *N*-Et group in every case in which nitration took place. Treated under a bell jar with  $NO_2$ , A gave, after 5 weeks, prisms of *4-nitro-2-methylphenylurethan* (B), m.  $135^\circ$ , sol. in most org. solvents except ligroin. Dissolved in  $CCl_4$ , AcOH, or  $Et_2O$ , satd. with  $NO_2$ , A gave almost no B after several months. Cold fuming  $HNO_3$  (d. 1.5) (warmed later to complete the reaction) gave with A *4,6-dinitro-2-methylphenylurethan* (C), fine needles from alc., m.  $159-60^\circ$ . C was also formed when fuming  $HNO_3$  was shaken continuously for 1 month with a 10% soln. of A in  $CCl_4$ ; with AcOH as solvent, C was formed only at water-bath temp.  $2,6-Me(O_2N)C_6H_3NH_2$  was condensed with  $ClCO_2Et$  in PhH by  $CaCO_3$ ; the *6-nitro-2-methylphenylurethan* (D), almost colorless prisms, m.  $131^\circ$ , is difficultly sol. in ligroin. Similarly made, *5-nitro-2-methylphenylurethan* (E), m.  $137^\circ$  (Vittenet, *Bull. soc. chim.* [3] 21, 592(1889)), gives  $129^\circ$  and  $127^\circ$  as the m. ps. of E and B, resp. C was obtained by nitrating either B or D with fuming acid; E, under these conditions, gives *4,5-dinitro-2-methylphenylurethan*, m.  $193-4^\circ$ .

B. H. NICOLET

**Action of the oxides and the oxy acids of nitrogen on ethylphenylurethan.** HUGH RYAN and ANNA CONNOLLY. *Sci. Proc. Roy. Dublin Soc.* 17, 125-30(1923).—The nitration of  $PhNEtCO_2Et$  (A) with  $NO_2$  in  $CCl_4$ , gave *4-nitrophenylethylurethan*, m.  $55^\circ$ , and a little *2,4-dinitrophenylethylurethan*, m.  $88^\circ$ . Fuming acid gave the same products. The use of  $HNO_3$  and  $H_2SO_4$  together gave, instead, dinitro- and trinitrophenylurethans, with loss of Et. Considerable detail is given.

B. H. NICOLET

**Action of the oxides and the oxy acids of nitrogen on phenylbenzylurethan.** HUGH RYAN and JAMES L. O'DONOVAN. *Sci. Proc. Roy. Dublin Soc.* 17, 131-7(1923).—*Phenylbenzylurethan* (A), oil, not further described, exposed to gaseous  $NO_2$  for some days, gave some trinitro deriv. (D) (2,4,4'?), m.  $110-1^\circ$ . A in AcOH, satd. with  $NO_2$  and let stand for some months, gave *4-nitrophenylbenzylurethan* (B), m.  $70-1^\circ$ , also obtained from A and fuming  $HNO_3$  at  $-5^\circ$ . Using fuming  $HNO_3$  and  $H_2SO_4$  at  $-10^\circ$ , a *tetranitro deriv.* (C), m.  $126-37^\circ$ , was obtained; at somewhat higher temps., the nitration gave a *pentanitrophenylbenzylamine*, silky needles, m.  $274^\circ$ , and a *compd.*, yellow felted needles, m.  $264^\circ$ , which was either a *pentanitro deriv.* of A or a *trinitrophenylbenzylamine*. After some months' standing, fuming  $HNO_3$  with 10% solns. of A in AcOH or  $CCl_4$  gave B. Direct nitration of A with fuming acid gave rather impure D and C. *Phenyl-*p*-nitrobenzylurethan*, from the reaction product of  $PhNH_2$ ,  $p-O_2NC_6H_4CH_2Cl$ , and  $ClCO_2Et$ , formed almost colorless rhombic plates, m.  $68-9^\circ$ .

B. H. NICOLET

**The action of the oxides and the oxy acids of nitrogen on the phenylureas.** HUGH RYAN and PETER K. O'TOOLE. *Sci. Proc. Roy. Dublin Soc.* 17, 139-55(1923).—Fuming  $HNO_3$  (d. 1.51), with or without  $H_2SO_4$ , gave with  $PhNHCONH_2$  (A), *2,4-dinitrophenylisourea* (B), m.  $164^\circ$  (decompn.) (Reudler, *C. A.* 8, 2373, gave  $154-7^\circ$  as the m. p.). Let stand in AcOH or alc. 2 months with excess  $HNO_3$ , A gave only the nitrate; in  $CCl_4$ , B was formed when 6 mols.  $HNO_3$  were used, but with  $NO_2$  or  $N_2O_5$  at room temp.,  $O_2NC_6H_4OH$  resulted.  $(PhNH)_2CO$  (C) gave with  $N_2O_5$  in AcOH, the *dinitrosamine* (D) cream-colored needles, decomp.  $103^\circ$ . The action of  $NO_2$  on C in AcOH, gave D and the 4,4'-( $NO_2$ )<sub>2</sub> deriv. of C, the latter also obtained by long standing of D in AcOH with fuming  $HNO_3$ . Formation of the sym. tetra- $NO_2$  deriv. of C is also discussed in detail.  $Ph_2NCONH_2$  (E), obtained in excellent yield by passing  $NH_3$  for 15 mins. into  $Ph_2NCOCl$  in hot MeOH, gave with  $N_2O_5$  in AcOH impure ( $p-O_2NC_6H_4$ )<sub>2</sub>NCONIINO, m.  $146^\circ$ . Cold fuming  $HNO_3$  converted E to the 2,4,2',4'-( $NO_2$ )<sub>4</sub> deriv.  $Ph_2NCONHPh$  (F) gave with  $N_2O_5$  or  $NO_2$  in AcOH at room temp., a *trinitro deriv.* (G), slightly yellow leaves, m.  $205-6^\circ$ , slightly sol. in  $Et_2O$ ,  $CHCl_3$ , or

$\text{CCl}_4$ , more so in alc. or  $\text{AcMe}$ . Nitrated for 2 months in  $\text{AcOH}$ , *F* gave *G*, and a more sol. *dinitro deriv.*, yellow prisms, m.  $190-1^\circ$ . In  $\text{CCl}_4$ , both these and a *pentanitro deriv.*, yellow crystals, decomp. from  $180^\circ$ , m.  $235-6^\circ$  (decompn.), were formed.

B. H. NICOLET

**Action of the oxides and the oxy acids of nitrogen on phenylmethylurea.** HUGH RYAN AND MICHAEL J. SWEENEY. *Sci. Proc. Roy. Dublin Soc.* 17, 157-62 (1923).—Nitration of  $\text{PhNMeCONH}_2$  under a wide range of conditions gave no urea  $\text{NO}_2$  derivs., but only products derived from  $\text{PhNHMe}$ , ranging from this to tetryl. B. H. N.

**Comparative study of phenylphosphonic acids and phenylarsonic acids substituted in the ring.** D. R. NIJK. *Rec. trav. chim.* 41, 461-500 (1922).—The purpose was (1) to elaborate methods that lead easily to the prepn. of the 3 isomeric  $\text{H}_2\text{NC}_6\text{H}_4\text{PO}_3\text{H}_2$ ; (2) to compare the properties of these acids with the analogous  $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$ ; and (3) to exam. the influence that atoms and groups introduced into the  $\text{C}_6\text{H}_5$  ring exercise on the stability of aminophenylphosphonic and aminophenylarsonic acids thus substituted. The prepn. of  $\text{PhPO}_3\text{H}_2$  (*A*) (Michaelis, *Ann.* 181, 265, 294 (1878)), from  $\text{C}_6\text{H}_6$  and  $\text{PCl}_3$ , giving  $\text{PhPCl}_2$ , which in turn with  $\text{Cl}_2$  gives  $\text{PhPCl}_4$  and this in turn with  $\text{H}_2\text{O}$  gives *A*, is fully described. *A* on nitration (Benzinger, *Ann.* 188, 276, 282 (1877)) gives  $3\text{-O}_2\text{NC}_6\text{H}_4\text{PO}_3\text{H}_2$  (*B*) and this on reduction the corresponding  $3\text{-NH}_2$  acid (*C*). The constitution of *B* and *C* was proved indirectly (Berthelm, Benda, *C. A.* 6, 491; van Dorssen, *C. A.* 5, 679) by converting *C* into  $2,4,6,3\text{-Br}_3(\text{H}_2\text{N})\text{C}_6\text{H}_2\text{IPO}_3\text{H}_2$  (*D*). 0.5 g. *D* + 20 cc.  $\text{H}_2\text{O}$  + 50 cc. concd.  $\text{H}_2\text{SO}_4$  was treated with steam ( $200-10^\circ$ ) at  $180-200^\circ$ , by which  $2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{NH}_2$  (*E*), m.  $118^\circ$ , was obtained. This proved that the  $\text{NO}_2$  in *A* is not in the *p*-position as suggested by Schenk and Michaelis (*Ann.* 260, 20 (1890)). In the nitration of  $\text{C}_6\text{H}_6$  derivs. several isomers are usually formed. When the nitration product of *A* was fractionally crystd. until the m. p. of the residue on evapn. was lower than that of *B* this fraction was reduced and the  $\text{NH}_2$  deriv. brominated as with *D*. On distg. with steam in  $\text{H}_2\text{SO}_4$  soln. *E* alone was obtained. The  $2,4$ - and  $2,6\text{-Br}_2\text{C}_6\text{H}_3\text{NH}_2$  that would have been formed if the *o*- and *p*-isomers of *B* had been present were not found (cf. v. D., *l. c.*). This proved that nitration of *A* gives *B* exclusively. In order to obtain a deriv. of *A* in which the  $\text{PO}_3\text{H}_2$  group is *p*- to  $\text{NH}_2$   $3\text{-nitro-4-aminophenylphosphonic acid}$  (*F*) was prepd. thus:  $p\text{-ClC}_6\text{H}_4\text{PCl}_2$  (Michaelis, *Ann.* 293, 223 (1896)), obtained from  $\text{PhCl} + \text{PCl}_3 + \text{AlCl}_3$ , treated with  $\text{Cl}_2$  gave  $\text{ClC}_6\text{H}_4\text{PCl}_2$ , which with  $\text{H}_2\text{O}$  gave  $4\text{-ClC}_6\text{H}_4\text{PO}_3\text{H}_2$  (*G*), m.  $181^\circ$ ; *G* on nitration gave the  $3\text{-NO}_2$  deriv., whose  $\text{NH}_4$  salt heated in a sealed tube in concd.  $\text{NH}_4\text{OH}$  gave *F* as dark yellow spangles, m.  $231^\circ$  (decompn., giving  $o\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  (*H*)). *F* in  $\text{HCl}$  with  $\text{Br-H}_2\text{O}$  ppts. yellow  $2,4,6,2\text{-Br}_3(\text{O}_2\text{N})\text{C}_6\text{H}_2\text{NH}_2$ , m.  $127-8^\circ$ , which proves that the  $\text{PO}_3\text{H}_2$  group *p*- to  $\text{NH}_2$  is replaced by  $\text{Br}$  like the groups  $\text{AsO}_3\text{H}_2$ ,  $\text{SO}_3\text{H}$ ,  $\text{CO}_2\text{H}$ , etc. In feebly acid soln. *F* decomp., giving  $\text{H}_3\text{PO}_4$  + *H*; on heating at  $100^\circ$  with concd.  $\text{HCl}$  it decomp., giving a yellow sirup contg. *II*. Attempts to obtain *o*- or *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{PO}_3\text{H}_2$  (*I*) and (*J*) by melting aromatic amines or their derivs. with  $\text{H}_3\text{PO}_4$ , as Béchamp (*Compt. rend.* 56, 1172 (1863)) did in the prepn. of aromatic arsonic acids, are described but gave negative results. Attempts to synthesize aromatic phosphonic acids from aromatic diazonium compds. and phosphites or their derivs. by a process like that used by Bart-Schmidt with aromatic arsonic and stibonic acids failed. Since nitration of *A* gave only *B*, N. attempted to obtain *I* and *J* from *C* by a roundabout method which consisted in protecting the  $\text{NH}_2$  against oxidation and then nitrating. For this purpose *C* was treated with  $\text{ClCO}_2\text{Et}$  according to the Schotten-Baumann method, which gave *m-carbethoxyaminophenylphosphonic acid* (*K*),  $\text{C}_6\text{H}_4(\text{PO}_3\text{H}_2)\text{NHCO}_2\text{Et}$ , m.  $140^\circ$ . *K* in glacial  $\text{AcOH}$  was nitrated at  $15^\circ$  and then treated slowly with  $\text{Ac}_2\text{O}$  at the same time. After 24 hrs. the  $\text{AcOH}$  was distd. off *in vacuo*, the brown sirup was extd. with petroleum ether and the residue dissolved in a mixt. of  $\text{Et}_2\text{O}$  and  $\text{Me}_2\text{CO}$

(4:1). After considerable further trouble *mononitro-3-carbethoxyaminophenylphosphonic acid* (*L*) was sepd. as bright yellow needles, m.  $165^{\circ}$  (decompn.) that explode on heating. 15 g. *L* boiled 15 mins. with 40 cc. concd. HCl evolved  $\text{CO}_2$  and on evapn. sepd. *mononitro-3-aminophenylphosphonic acid* (*M*) as dark yellow needles, m.  $185^{\circ}$ . Unsuccessful attempts to det. whether the  $\text{NO}_2$  in *M* is in the 2- or 4-position are described. *G* does not react with  $\text{NH}_4\text{OH}$  alone but in the presence of Cu powder *J* was obtained and shown to be stable in concd.  $\text{NH}_4\text{OH}$  soln., but the free acid is not stable in soln. *Derivs. of phenylarsonic acid*.—The method of Béchamp and Berthelm for prep.  $p\text{-I}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$  (*N*) by heating  $\text{PhNH}_2$  with  $\text{As}_2\text{O}_3$  was improved to increase the yield. The same method for obtaining  $5,2\text{-O}_2\text{N}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$  was corrected. The structure of *N* was proved. By nitration of  $\text{PhAsO}_3\text{H}_2$  (*O*) *N*, obtained only  $m\text{-O}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$  (*P*); the presence of the *o*- and *p*-isomers could not be demonstrated. With abs.  $\text{HNO}_3$  *O* is more difficult to nitrate than *A*, which Michaelis had already found to be true with fuming  $\text{HNO}_3$ . The constitution of *P* was proved by reducing it to  $m\text{-H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$  (*Q*), which in turn heated with  $\text{H}_2\text{SO}_4$  gave  $2,4,6\text{-Br}_3\text{C}_6\text{H}_2\text{NH}_2$ . The action of  $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{Cl}$  on solns. of arsenite does not give  $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$ . The analogy between the Sandmeyer-Gattermann reaction for obtaining aromatic  $\text{NO}_2$  compds. from benzenediazonium compds. and nitrites and the Bart-Schmidt reaction for the prepn. of phenylarsonic and phenylstibonic acids from benzenediazonium compds. and arsenites and antimonites, resp., is discussed. It was found that the case of  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{PO}_3\text{H}_2$  (Michaelis, Schenk, *Ann.* 260, 7(1890)), in which the  $\text{PO}_3\text{H}_2$  group is so loosely bound that it is easily sepd. from the  $\text{C}_6\text{H}_5$  ring in  $\text{H}_2\text{O}$ , giving  $\text{Ph-NMe}_2 + \text{H}_3\text{PO}_4$  is not an exceptional one. *N* has observed that phenylphosphonic acids in which the  $\text{H}_2\text{PO}_3$  group is *o*- or *p*- to the  $\text{NH}_2$  group are unstable acids. In  $\text{H}_2\text{O}$  they dissociate easily into the amine and  $\text{H}_3\text{PO}_4$ . It is only  $\text{NH}_2$  in the *o*- or *p*-position that causes this; in the *m*-position it does not cause it. In these compds. the  $\text{PO}_3\text{H}_2$  group is also easily replaced by Br. The fact that *J* is not obtained by fusion of  $\text{PhNH}_2$  with  $\text{H}_3\text{PO}_4$  is also in agreement with these facts. *C* is quite stable and behaves like all other phenylphosphonic acids previously described. It was found that the  $\text{NO}_2$  *o*- to  $\text{NH}_2$  does not diminish the stability of *C*. This property also exists in the aminophenylarsonic acids examd. *N* is a stable acid. The introduction of Br atoms *o*- and *p*- to the  $\text{NH}_2$  group does not diminish the stability of *Q*. In *N* the  $\text{AsO}_3\text{H}_2$  is easily liberated, giving  $\text{PhNH}_2$  and  $\text{H}_3\text{AsO}_4$ . In *Q* the presence of Br next to the  $\text{NH}_2$  increases the stability since dil. HCl does not sep. the  $\text{AsO}_3\text{H}$  group from *Q*.  $\text{AsO}_3\text{H}_2$  is easily replaced by Br in *o*- and *p*- $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$ ; thus  $5,2\text{-O}_2\text{N}(\text{H}_2\text{N})\text{C}_6\text{H}_3\text{AsO}_3\text{H}_2$  gives on treatment with  $\text{Br-H}_2\text{O}$   $2,6,4\text{-Br}_3(\text{O}_2\text{N})\text{C}_6\text{H}_2\text{NH}_2 + \text{H}_3\text{AsO}_4$ . A comparison of aromatic derivs. of  $\text{HNO}_3$ ,  $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$  shows that  $\text{PhNO}_2$ , *A* and *O* are stable compds. from which it is not easy to detach the acid group. Only  $\text{PO}_3\text{H}_2$  and  $\text{AsO}_3\text{H}_2$  can be detached by energetic means. But when an  $\text{NH}_2$  group is introduced *o*- or *p*- to the  $\text{NO}_2$ ,  $\text{PO}_3\text{H}_2$  or  $\text{AsO}_3\text{H}_2$  group the stability of the derivs. contg. the last 2 groups is sharply changed; but in *o*- or *p*- $\text{O}_2\text{NC}_6\text{H}_4\text{NH}_2$  the  $\text{NO}_2$  remains firmly fixed in the ring. In this case the *J* is less stable than *N*. If, however, an  $\text{NH}_2$  is introduced into the compds. in the *m*-position the bonds do not undergo any notable change; it is necessary to apply more energy to detach the radicals of the inorg. acids.

E. J. WITZEMANN

**Chloroacetyl-*p*-anisidine and its nitro derivatives.** FRÉDÉRIC REVERDIN. *Helvetica Chim. Acta* 6, 87-93(1923).—Chloroacetyl-*p*-anisidine (*A*) was prepd. in 91% yield, essentially according to Jacobs and Heidelberger (*C. A.* 11, 2329). Fuming  $\text{HNO}_3$ , added slowly to a 10% soln. of *A* in AcOH at  $10\text{-}5^{\circ}$ , gave 80-2% of the 3-nitro deriv. of *A* ( $-\text{OMe} = 1$  throughout), yellow needles, m.  $104^{\circ}$ , readily sol. in alc. and AcOH, and particularly in hot PhH. Hydrolysis of the acyl group in *B* with hot concd.  $\text{H}_2\text{SO}_4$

(incomplete after 5 hrs. at 100°) was unusually difficult; but was exceptionally easy with 4% KOH; other derivs. of *A* showed similar results. Addn. of *B* to fuming HNO<sub>3</sub> at 15–30° gave 95% of the *2,3-dinitro deriv.* (*C*), of *A*, prismatic needles, m. 172°; a small amt. of the *2,5-dinitro deriv.*, m. 125°, was also formed. *C* in H<sub>2</sub>SO<sub>4</sub> nitrated with fuming HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> gave 40% of the *2,3,5-trinitro deriv.* (*D*), needles, m. 245–6°. The reaction of these compds. with amines is not smooth. *B* dissolved in PhNH<sub>2</sub> gave *3-nitro-4-[anilinoacetyl]anisole*, yellow plates, m. 143°. The products obtained from *C* and *D* with PhNH<sub>2</sub> are not yet identified. The methods described have been worked out with great care, and interesting comparisons with related acyl derivs. are made.

BEN H. NICOLET

• Synthesis of  $\beta$ -keto bases from aliphatic-aromatic ketones, formaldehyde, and secondary amines. C. MANNICH AND D. LAMMERING. *Ber.* 55B, 3510–26(1922); cf. *C. A.* 16, 2497.—In view of the importance of plant syntheses, it is interesting to find that simple amine salts give, with CH<sub>2</sub>O, complicated N compds. under comparatively mild conditions. M. and L. have studied the reaction between sec. amines, CH<sub>3</sub>O and aliphatic-aromatic ketones. The reaction is as follows: MeOC<sub>6</sub>H<sub>4</sub>COMe + CH<sub>2</sub>O + HNC<sub>3</sub>H<sub>7</sub>·HCl = H<sub>2</sub>O + MeOC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>2</sub>NC<sub>3</sub>H<sub>7</sub>·HCl. The reaction in most cases proceeds easily and with good yields. It is carried out by boiling a mixt. of the HCl salt of the amine with concd. CH<sub>2</sub>O soln. and the ketone for 1 hr.; better still by warming the amine salt and the ketone with paraformaldehyde in alc. A large no. of  $\beta$ -keto bases can be thus prepd., inasmuch as both the amine and the ketone may be varied widely. In exceptional cases the reaction does not proceed normally. The keto bases so obtained in the form of their solid HCl salts are relatively stable. Aq. solns. on boiling decomp. to give the amine and an unsatd. ketone. Superheated steam or dry distn. *in vacuo* produces the same effect. *E. g.*, *p*-MeOC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> gives NHMe<sub>2</sub>·HCl and MeOC<sub>6</sub>H<sub>4</sub>COCH<sub>2</sub>CH<sub>2</sub>, the latter in poor yield due to polymerization. The vinyl compd. on reduction, yields propionanisone. Some of the free keto bases are solid; the liquid ones cannot be distd. *in vacuo*. The keto bases give normal oximes except in case of the NMe<sub>2</sub> derivs. The keto groups may be reduced by various well known methods. This synthesis of  $\beta$ -keto bases makes possible the synthesis of compds. of the type of adrenaline, tyramine, hordenine, etc., but with the N in the  $\gamma$ -position. The corresponding homolog of adrenaline caused no rise of blood pressure, but a fall. However, the C<sub>6</sub>H<sub>5</sub> derivs. of the type PhCOCH<sub>2</sub>CH<sub>2</sub>NC<sub>3</sub>H<sub>7</sub> are local anesthetics. Replacement of the Ph group by other groups also gave anesthetic compds. Reduction of the keto bases to the  $\beta$ -NH<sub>2</sub> alics. caused loss of anesthetic properties, but benzylation caused marked anesthesia. The Bz group and the N are here in the same positions as in cocaine. Some of these compds. produced are more anesthetic than cocaine, but are irritating. The *p*-H<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H esters of these 1,3-amino alics. are anesthetics.  $\beta$ -Piperidinoethyl phenyl ketone hydrochloride, obtained by boiling in abs. alc. C<sub>6</sub>H<sub>11</sub>N·HCl, paraformaldehyde and PhCOMe, leaflets from EtOH-Me<sub>2</sub>CO, m. 192–3°, readily sol. in H<sub>2</sub>O, MeOH, CHCl<sub>3</sub>, difficultly in alc., Me<sub>2</sub>CO, and EtOAc. Boiling in aq. soln. causes decompn. with formation of CH<sub>3</sub>:CH<sub>2</sub>COPh. The free base is a nondistillable oil. *Picrate*, needles from HOAc, m. 180.5°. *Oxime*, needles from dil. alc., m. 143°. 1,6-Dipiperidino-3,4-diphenylhexane-3,4-diol ( $\alpha$ - and  $\beta$ -forms), prepd. by placing a moist Et<sub>2</sub>O soln. of the above ketone in contact with activated Al and extg. with Et<sub>2</sub>O in a Soxhlet, needles from CHCl<sub>3</sub>, m. 238° with brown coloration. *HCl salt*, m. 270°. This is the  $\alpha$ -form. The  $\beta$ -form, obtained from the mother liquors of the  $\alpha$ -form by treatment with HCl, followed by alkali, plates from alc., m. 115°. Probably one of these forms is the *dl*-, the other the *meso*-compd. [ $\beta$ -Piperidinoethyl]phenylcarbinol, by reduction of the HCl salt of the corresponding ketone base in H<sub>2</sub>O by H and palladiumized charcoal; *HCl salt*, crystals from CHCl<sub>3</sub>-EtOAc,

m. 138°. Treatment with  $\text{NH}_4\text{OH}$  gives an oil crystg. from  $\text{MeOH}$ , in leaflets, m. 68-9°. *Picrate*, needles, m. 103°. The same is obtained by reduction with  $\text{Zn}$  dust and  $\text{HI}$ . *Hydrochloride of benzoate*, by the action of  $\text{BzCl}$  on the base in  $\text{CHCl}_3$ , flat needles, m. 170°, is strongly anesthetic. *p-Nitrobenzoyl ester*, by boiling the base in  $\text{C}_6\text{H}_6$  with  $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$ , brown needles from alc., m. 104°. *p-Aminobenzoate*, from the  $\text{NO}_2$  compd. with  $\text{Sn}$  and  $\text{HCl}$  at 40°, needles from ether, m. 118°; solns. of the  $\text{HCl}$  salt are strongly anesthetic.  *$\beta$ -Tetrahydroisoquinolinoethyl phenyl ketone hydrochloride*, by boiling tetrahydroisoquinoline- $\text{HCl}$  in abs. alc. with paraformaldehyde and  $\text{PhCOMe}$ , m. 188°. The free base is a viscous oil, crystg. in an ice mixt. *N,N'-Bis-[ $\beta$ -benzoylethyl]piperazine*, prepd. in a similar manner from piperazine; the  $\text{HCl}$  salt turns brown at 190° without melting; the free base, by treatment with  $\text{NH}_3$ , crystals from 70% alc., m. 141°. *Picrate*, needles from  $\text{PhNO}_2$ , decomp. above 190°. *Dioxime*, m. 245°.  *$\beta$ -Dimethylaminoethyl p-methoxyphenyl ketone*, prepd. from acetanisone, paraformaldehyde, and  $\text{Me}_2\text{NH}\cdot\text{HCl}$ , crystals as the  $\text{HCl}$  salt, needles from alc. m. 181°. *Picrate*, needles, m. 145°. By heating the  $\text{HCl}$  salt under 20 mm. at 180°, it decomp. to  $\text{Me}_2\text{NH}\cdot\text{HCl}$  and vinyl anisyl ketone, m. 19°, unstable in liquid form, undergoing polymerization; *dibromide*, by the action of  $\text{Br}$  in  $\text{CHCl}_3$ , prisms from ligroin, m. 71°. Alc.  $\text{PhNHNH}_2$  boiled with the ketone gives crystals, m. 105°, probably of 1-phenyl-3-p-methoxyphenylpyrazoline. *Et anisyl ketone*, prepd. by reduction of the vinyl ketone, is identical with Klages' product (*Ber.* 35, 2262(1902)).  *$\beta$ -Dimethylaminoethyl p-hydroxyphenyl ketone*, prepd. from the corresponding  $\text{MeO}$  compd. by boiling with  $\text{HI}$ . *Hydroiodide*, light yellow leaflets from alc., m. 205°. Alkalies do not cause sepn. of the free base from its aq. solns. [ *$\beta$ -Dimethylaminoethyl]-p-anisylcarbinol hydrochloride, by reduction of the keto base with  $\text{H}$  and  $\text{Pd}$ , needles from  $\text{CHCl}_3\text{:EtOAc}$ , m. 203-4°. Free base,  $b_{10}$  146-8°, m. 53°. *Benzoate*, from the carbinol and  $\text{BzCl}$  in  $\text{CHCl}_3$ ; on addn. of  $\text{EtOAc}$ , the  $\text{HCl}$  salt, m. 174°, seps. It is a powerful anesthetic.  *$\beta$ -Piperidinoethyl p-anisyl ketone*, from  $\text{C}_6\text{H}_{11}\text{N}\cdot\text{HCl}$ , acetanisone, and paraformaldehyde;  $\text{HCl}$  salt, needles, m. 216°. The free base is an oil which solidifies in an ice mixt. *Picrate*, short needles, m. 165°. *Oxime*, needles from alc., m. 136°. *N,N'-Bis-[ $\beta$ -p-anisylethyl]piperazine*, from piperazine,  $\text{HCl}$ , acetanisone, and paraformaldehyde. The  $\text{HCl}$  salt becomes brown at 150° without melting. Free base, yellowish leaflets, m. 173°, turning brown at 171°.  *$\beta$ -Piperidinoisopropyl p-anisyl ketone*, prepd. in a similar manner from  $\text{Et}$  p-anisyl ketone;  $\text{HCl}$  salt, leaflets from abs.  $\text{EtOH-Me}_2\text{CO}$ , m. 178°. The free base is an oil. *Oxime*, m. 94°.  *$\beta$ -Dimethylaminoethyl 3,4-dimethoxyphenyl ketone*, by heating acetoveratrone,  $\text{Me}_2\text{NH}\cdot\text{HCl}$ , and paraformaldehyde in abs. alc., is a viscous oil. The  $\text{HCl}$  salt m. 181-2°; *picrate*, needles, m. 157°.  *$\beta$ -Dimethylaminoethyl 3,4-dihydroxyphenyl ketone hydroiodide*, from the above  $\text{MeO}$  compd. with  $\text{HI}$ , light yellow crystals, m. 196°. Alkalies give no ppt. *1-[ $\gamma$ -Dimethylaminopropyl]-3,4-dimethoxybenzene hydrochloride*, by reduction of the  $\text{HCl}$  salt of the corresponding keto base by  $\text{H}$  and  $\text{Pd}$ , needles from  $\text{Me}_2\text{CO}$ , m. 196°. Free base, colorless and odorless oil,  $b_{20}$  161-4°.  *$\beta$ -Piperidinoethyl 3,4-dimethoxyphenyl ketone*, prepd. from  $\text{C}_6\text{H}_{11}\text{N}\cdot\text{HCl}$ , acetoveratrone, and paraformaldehyde;  $\text{HCl}$  salt, prisms, m. 183°. Free base m. 113°. *Picrate*, m. 180°. *Oxime*, needles from alc., m. 168°. *N,N'-Bis-[ $\beta$ -veratroylethyl]piperazine*, prepd. in a similar manner from piperazine;  $\text{HCl}$  salt, short needles from 10%  $\text{HCl}$ , decomp. at 150° with brown coloration. Free base, yellow needles, m. 188°.  *$\beta$ -Diethylaminoethyl veratryl ketone hydrochloride*, prepd. from  $\text{Et}_2\text{NH}\cdot\text{HCl}$  by the usual method, needles from  $\text{EtOAc}$ , m. 140-1°. The free base is a nondistillable oil. *Picrate*, m. 136°; *oxime*, m. 104°. *1-Piperidino-2,3-diphenyl-3-propanone*, prepd. from desoxybenzoin,  $\text{C}_6\text{H}_{11}\text{NH}\cdot\text{HCl}$ , and paraformaldehyde, crystals from 90% alc., m. 91°. The  $\text{HCl}$  salt is hygroscopic, but the  $\text{HNO}_3$  salt forms difficultly sol. needles, m. 117°.  *$\beta$ -[ $\omega$ -Dimethylaminopropyl]tetralin*, prepd. from acetotetralin;  $\text{HCl}$  salt,*

needles from  $\text{Me}_2\text{CO}$ , m.  $170^\circ$ . The free base is an oil; *picrate*, needles, m.  $156^\circ$ . *ω-Dimethylaminoethyl-β-ar-tetrahydronaphthylcarbinol*, prepd. by reducing the HCl salt of the above keto base with H and Pd; *HCl salt*, leaflets from  $\text{Me}_2\text{CO}$ , m.  $163^\circ$ . The free base is an oil. *β-[ω-Piperidinopropyl]-tetralin; HCl salt*, needles from  $\text{Me}_2\text{CO}$ , m.  $170^\circ$ , crystals from water with water of crystal, and m.  $85^\circ$ . This free base is an oil. *Nitrate*, difficultly sol. in water, m.  $134-5^\circ$ . *Oxime HCl salt*, silky needles from dil. alc., m.  $211^\circ$ . E. H. VOLWILER

**Preparation of heliotropin from camphor oil.** SHIOICHIRO NAGAI. *J. Chem. Ind. (Japan)* 25, 52-60(1922).—A supplemental report (cf. C. A. 16, 4182). During isomerization of safrole, if 1 part of safrole, 0.5 part of KOH and 1 part alc. are used at  $94-95^\circ$  for 4-5 hrs., alc. KOH will sep. out on the top of the isosafrole, which can be used for 3-4 times without practically affecting the yield (83%). At the 4th repetition, the yield is considerably lowered. In case solid KOH alone is used, if the proportion is taken as reported previously, the solidified KOH settles at the bottom and also can be used several times. At the end of the 7th usage, the yield was still as high as 93%, almost equal to the first. With a view of preventing further oxidation of heliotropin to piperonylic acid during the oxidation of isosafrole by  $\text{K}_2\text{Cr}_2\text{O}_7$ , inert org. solvents ( $\text{C}_6\text{H}_6$ , PhMe, xylene,  $\text{PhNO}_2$ ,  $\text{CS}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ ) were first added to the safrole before introduction of the  $\text{K}_2\text{Cr}_2\text{O}_7$ . The results show practically no improvement, except a slight benefit in the case of heavy solvents. Thus far, therefore, oxidation by inorg. agents has not given more than 40-50% yields. Electrolytic and  $\text{O}_3$  oxidation are contemplated. S. T.

**Dealkylation of mixed secondary bases by phosphorus pentachloride.** JULIUS V. BRAUN AND JOSEF WEISMANTEL. *Ber.* 55B, 3165-70(1922).—In previous work it had been established that for the reaction  $\text{R}'\text{R}''\text{R}'''\text{N} + \text{BrCN} = \text{R}'\text{Br} + \text{R}'' + \text{R}''' + \text{N}_2$ , the hydrocarbon radicals PhCH<sub>2</sub>, Me, Et, Pr, and Bu could be eliminated from a tert. amine with an ease corresponding to the order given. In the present work it is shown that exactly the same series holds for the elimination of hydrocarbon radicals

from sec. amines according to the reactions  $\text{R}'\text{R}''\text{NH} \xrightarrow[\text{heat}]{\text{PCl}_5} \text{R}'\text{R}''\text{NCOPh} \xrightarrow[\text{H}_2\text{O}]{\text{heat}} \text{R}'\text{R}''\text{NH} + \text{R}'\text{R}''\text{N} + \text{R}'\text{R}''\text{NCOH}$

$\text{NCCl}_2\text{Ph} \rightarrow \text{R}'\text{Cl} + \text{R}''\text{N} + \text{CCl}_2\text{Ph} \rightarrow \text{R}'\text{Cl} + \text{R}''\text{NH}_2$ . It is especially significant that the same series should hold since the BrCN reaction is carried out at  $0^\circ$  while the  $\text{PCl}_5$  reaction only goes at  $110-150^\circ$ . In the exptl. work there were prepd.: *methylbenzylbenzamide*, m.  $41^\circ$ , b<sub>10</sub>  $212^\circ$ ; *methylethylbenzamide*, b<sub>12</sub>  $183^\circ$ ; *ethylpropylbenzamide*, b<sub>12</sub>  $158^\circ$ ; *propylbutylbenzenesulfonamide*, b<sub>12</sub>  $202^\circ$ ; *propylbutylamine*, b.  $134^\circ$  (*hydrochloride*, m.  $255^\circ$ ); *propylbutylbenzamide*, b<sub>12</sub>  $175-8^\circ$ . O. B. HELFRICH

**The iodation of *m*-hydroxybenzoic acid.** P. H. BEIJER. *Rec. trav. chim.* 41, 701-2(1922).—Wieselsky (*Ann.* 174, 105(1874)) iodated *m*- $\text{HO}(\text{C}_6\text{H}_4)\text{CO}_2\text{H}$  (A) in EtOH with I + HgO and obtained a mono-I deriv. and a little iodophenol. The m. p. and constitution were not given. In brominating A B. (C. A. 16, 1230) obtained only 3,4-(HO)BrC<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H, while with Cl A gives 2 isomeric mono-Cl derivs. On repeating W.'s prepa. B. obtained 4,3-I(HO)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (B) as white needles, m.  $226-8^\circ$ (decompn.). A little iodophenol was also obtained. The constitution of B was proved by prep. it from 3,4-HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (C). On reduction with alk. Na<sub>2</sub>S C gives the corresponding NH<sub>2</sub> deriv. which was diazotized and treated with KI, giving a product identical with B. 3,6-HO(O<sub>2</sub>N)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H treated as with C gave 6,3-(HO)C<sub>6</sub>H<sub>3</sub>CO<sub>2</sub>H (cf. Limpriicht, *Ann.* 263, 234(1891)), not identical with B. E. J. WITZEMANN

**Phenylalanine series.** II. Synthesis of 3,4-dihydroxyphenylethylamine. E. WASER AND H. SOMMER. *Helvetica Chim. Acta* 6, 54-61(1923); cf. C. A. 16, 81.—Nitration of tyramine (*p*- $\text{HO}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_2\text{NH}_2$ ) suspended in 7 parts H<sub>2</sub>O, at  $0^\circ$ , with 3.5 parts 56%  $\text{HNO}_3$ , gave 88% of 3-nitrotyramine (A), sepg. as the nitrate, yellow

needles from  $H_2O$ , m.  $208^\circ$  (decompn.). *A* forms yellow to orange prisms, m.  $217^\circ$  (decompn.), sol. 0.5% in cold  $H_2O$ ; it does not give the Millon reaction. The *hydrochloride*, very sol. in  $H_2O$ , m.  $214.5^\circ$ ; the *chloroplatinate*, needles, decomp.  $265^\circ$ ; the *picrate*, prisms, m.  $204^\circ$  (decompn.). A by-product of *A* was *3,5-dinitrotyramine*, orange-red powder, decomp.  $290^\circ$ ; its *nitrate*, prisms, m.  $163^\circ$  (decompn.); the *picrate* m.  $196^\circ$ . *A* reduced with Sn and HCl (better, 100% yield, with Pt black and  $H_2$ ) gave *3-aminotyramine* (*B*), m.  $145-7^\circ$ , sol. 0.6% in cold  $H_2O$  and 2% in hot, sepg. as *B.H\_2O*, m.  $127^\circ$ ; *dihydrochloride*, needles, m.  $305^\circ$  (decompn.); *monopicrate*, dark brown prisms, m.  $204.5^\circ$  (decompn.); *dipicrate*, light brown leaflets, m.  $212^\circ$  (decompn.). *B* was best diazotized with  $Ba(NO_3)_2$  in a soln. contg.  $3H_2SO_4$ , and the unfiltered mixt. poured into an excess of boiling satd.  $CuSO_4$  soln. Isolation of the product, *3-hydroxytyramine* (*C*) is preferably conducted with protection from air. The hydrochloride of *C* formed needles, very sol. in  $H_2O$ , m.  $237^\circ$  (decompn.); the *picrate* m.  $189^\circ$  (decompn.). *C* gives the Millon test, reduces cold  $NH_2AgNO_3$ , and shows characteristic color reactions with  $FeCl_3$  followed by various alkalis. III. Hydrogenation of tyrosine. E. WASER AND E. BRAUCHLI. *Ibid* 199-205.—The failure of Weinlagen (*C. A.* 12, 2083) to hydrogenate *l*-tyrosine (*A*) may have been due to impurities. With a special Pt black (cf. *C. A.* 15, 2077) under minutely described conditions, very pure *A* (dissolved in 2HCl) was hydrogenated completely in 90 hrs. Neutral and alk. solns. worked less well. *l*-Hexahydrotyrosine (*B*) sol. 4% in cold  $H_2O$ , forms tiny needles, m.  $307^\circ$  (decompn.) (very rapid heating in sealed capillary tubes); it is stable toward alk.  $KMnO_4$  and toward  $Br_2$  in  $CHCl_3$ , and gives no Millon test. The *hydrochloride*, very sol. leaflets or needles, m.  $249^\circ$  (decompn.); the *chloroplatinate*,  $B_2.H_2PtCl_6.3H_2O$ , sol. yellow needles, m.  $204^\circ$  (decompn.); the *picrate*, yellow needles, m.  $196^\circ$  (decompn.); *monobenzoyle* deriv., difficultly sol. in  $H_2O$ , m.  $186^\circ$ ; *l*-3-phenyl-5-hexahydrobenzylhydantoin, from *B* and  $PhNCO$  in alk. soln., followed by heating with 50%  $H_2SO_4$  to close the ring, needles from  $Et_2O$ , m.  $159-61^\circ$ . While *A* in 4% HCl showed  $[\alpha]_D^{20} = -11.11$ , *B*, under the same conditions, showed  $[\alpha]_D^{20}$  13.18. IV. Rotation dispersion of tyrosine and some of its derivatives. E. WASER. *Ibid* 206-14.—A surprisingly large majority of the derivs. of *l*-tyrosine (*A*) are *d*-rotatory, though their prepn. has not involved the asym. *C* directly. Karrer and Kease (*C. A.* 14, 1663, 2165) have shown, in the case of a series of reaction products of glutamic acid, that, neglecting the sign of  $[\alpha]_D$ , the rotation dispersion of these compds. showed const. direction except in those cases where a Walden inversion could be shown to have taken place. W. gives values of  $[\alpha]$  for 10 derivs. of *A* at 5 different wave lengths, and concludes that the rule of K. and K. does not apply here. The prepn. of *dl*-tyrosine (*B*) by refluxing *A* for 3 days with 33% NaOH is described. Fed to dogs, *B* was completely utilized, as no *d*-tyrosine could be isolated from the urine.

BEN H. NICOLET


Asymmetric syntheses. EMIL ERLÉNMEYER AND HANS ERLÉNMEYER. *Biochem. Z.* 133, 52-62(1922).—When cinnamic acid reacts with Br in the presence of glucose, ZnO and either  $ZnBr_2$  or  $ZnCl_2$ , a *l*-rotatory cinnamic acid dibromide results. If the Zn halide be omitted and ZnO be replaced by MgO or KOH, the dibromide is optically inactive. When levulose is substituted for glucose, a *l*-rotatory dibromide is obtained, even if the Zn halide be omitted or be replaced by NaCl. Substitution of *l*-arabinose for glucose gives a *d*-rotatory dibromide, substitution of sucrose a *l*-rotatory dibromide, and substitution of lactose an optically inactive dibromide. When  $\alpha$ -methylcinnamic acid reacts with Br in the presence of ZnO and fructose, a *l*-rotatory dibromide of the acid results. With the exception of lactose, the presence of an asym. sugar causes the synthesis of the dibromide to proceed asymmetrically.


JOSEPH S. HEPBURN

The catalytic ammonolysis of  $\beta$ -naphthol and chlorobenzene in the vapor state. A. M. HOWALD AND ALEXANDER LOWY. *Ind. Eng. Chem.* 15, 397-401(1923).—A

study of the direct action of  $\text{NH}_3$  on  $\beta$ -naphthol (*A*) and on  $\text{PhCl}$  (*B*) in the presence of catalysts. *A* was passed in the vapor state mixed with  $\text{NH}_3$  over various catalysts at definite temps. The yield of  $\beta\text{-C}_{10}\text{H}_7\text{NH}_2$  (*C*) was a function of the catalyst, temp., relative amts. of reacting compds. and the rate of flow over the catalyst. Alumina was the best catalyst, 30-5% yields of *C* being obtained under varying conditions. By passing *B* and  $\text{NH}_3$  over various catalysts, a max. yield of 7% of  $\text{PhNH}_2$  was obtained. Reduced metals of the Fe group were the only catalysts which formed appreciable yields of  $\text{PhNH}_2$ , and these catalysts rapidly became inactive, probably because of poisoning by the chlorides formed. Analogous expts. with  $\text{PhBr}$ ,  $\text{PhI}$  and  $p\text{-C}_6\text{H}_4\text{Cl}_2$  in the presence of Fe did not give promising results. C. C. DAVIS

**Univalent oxygen. I. Introduction.** STEFAN GOLDSCHMIDT. *Ber.* 55B, 3194-7 (1922).—References to previous work are given and attention is directed to the fact that the most illuminating results are to be obtained by working with the *hydroquinol ethers*. **II. Phenanthroxyls.** STEFAN GOLDSCHMIDT AND WALTER SCHMIDT. *Ibid.* 3197-3215.—The Me ether of phenanthrenehydroquinol (*A*) was prepd. by the action of  $\text{Me}_2\text{SO}_4$  on a KOH soln. of *A* in a H atm. Yield 7-12%. The product (*B*) m.  $103^\circ$ . The Et ether of *A* was prepd. by the action of  $\text{ZnEt}_2$  on *A* in abs.  $\text{Et}_2\text{O}$ . The product (*C*) was cryst. but no m. p. is given. The action of  $\text{ZnMe}_2$  on *A* gave only the di-Me ether of *A*, m.  $87^\circ$ . *A* gave with  $\text{Ac}_2\text{O}$  the monoacetate (*D*), m.  $170^\circ$  (decompn.). *B* and *C* were oxidized either by alk.  $\text{K}_2\text{Fe}(\text{CN})_6$  or  $\text{PbO}_2$  to colorless alkali-insol. products, (*B'*) and (*C'*), resp., giving in soln. a greenish yellow color. *D* was oxidized by  $\text{PbO}_2$  but the product formed colorless solns. in all solvents. G. considers *B'* and *C'* to be peroxides which dissociate in soln. to form free colored radicals *contg. univalent oxygen*. It is shown that dissociation in soln. takes about 2.5 hrs. to reach equil. and amts. to 37% for *B'* and 62% for *C'* at room temp. These measurements were made by detn. of the change in the apparent mol. wt., and by the deviation from Beer's law (cf. *Ann.* 381, 347). Both *B'* and *C'* were fairly stable toward O, only slowly forming phenanthrenequinone (*E*). Reduction by Zn and  $\text{HOAc}$ , HI, and  $\text{PhNHNH}_2$  reformed *B* and *C*. *B* gave *E* quant. from *C*. With  $\text{Ph}_3\text{C}$  there was reaction; the expected ether could not be crystd. out, but hydrolysis gave *C* and  $\text{Ph}_3\text{COH}$ . On the basis of

these results it seems that *B'* and *C'* are of the formula  and on dissoci-

ation give 2 , the latter to be called *9-alkoxy-10-phenanthroxyl*.

O. B. HELFRICH

The absorption spectra of pyrrole and its derivatives. The influence of methyl groups upon the absorption spectra of pyrrole and its derivatives. G. KORSCHUN AND C. ROLL. *Bull. soc. chim.* 33, 55-67 (1923).—1,2,5-Trimethylpyrrole and esters of the following pyrrole derivs. were prepd. and their absorption spectra in dil. alc. soln. studied: 2,5-dimethyl-, 2,3,5-trimethyl- and 1,2,3,5-tetramethylpyrrole-4-carboxylic acid; 2,5-dimethyl- and 2,3,5-trimethyl-1-aminopyrrole-4-carboxylic acid; 2,5-dimethyl- and 1,2,5-trimethylpyrrole-3,4-dicarboxylic acid; 2,5-dimethyl- and 2,3,5-trimethyl-1-tetridopyrrole-4-carboxylic acid. It was observed that when a Me group is introduced into a pyrrole deriv. in position 1, the absorption spectrum is displaced toward the ultra-violet, and at the same time, if the deriv. has 2 absorption bands, they unite into a single one. When Me is introduced into position 3, the spectrum is displaced toward the red, and at the same time the primary band is lowered and the secondary raised. Me in positions 2 and 5 of the 1,2,5-trimethylpyrrole mol. displaces the spectrum toward the



red. Three Me groups introduced in positions 1, 2 and 5 increase the intensity of the absorption bands very slightly.

T. S. CARSWELL

"So-called" isomerism in the isatin series. A. HANTSCH. *Ber.* **55B**, 3180-94 (1922).—By working with pure compds. H. obtains results which force him to conclude that there is no isomerism in the isatin series (cf. Heller, *C. A.* **16**, 1099, 3653), and which verify his own earlier expressed views (*C. A.* **15**, 3482). It is shown that the hydrolysis of isatin alkyl ethers gives dipol. isatoids and not isomeric members of the isatin series. The mol. wt. detns. were made in PhOH. H. claims that much of Heller's confusion was caused by impure chemicals. It was found that pure Ag salts in the isatin series were always red-violet and that when gray salts were obtained it was due to the presence of Ag<sub>2</sub>O. Ignorance of this fact was the basis of the claims of two structurally isomeric series, the *O*-salts and the *N*-salts. In the course of this work the following compds. were prepd.; isatin Me ether, m. 101°; Et ether, m. 52°; Prether, m. 72°; iso-Am ether, m. about 40°; 5-bromoisatin Me ether, m. 147°; 5-chloroisatin Me ether, m. 144°; 5-methylisatin Me ether, m. 131°; 5,7-dibromoisatin Me ether, m. 158°; 5,7-dimethylisatin Me ether, m. 137°; isatoid Me ether, m. 226°; Et ether, m. 228°; Pr ether, m. 189°; dimethylisatoid Me ether, m. 235°; tetramethylisatoid Me ether, m. 245°; chloroisatoid Me ether, m. 239°; bromoisatoid Me ether, m. 216°; isatin dianil, m. 210°; isatin benzoyloxime, m. 128°.

O. B. HELFRICH

Strychnine alkaloids. XXXIV. Preparation of isostrychnine. HERMANN LEUTCH AND RUDOLPH NITSCHKE. *Ber.* **55B**, 3171-4 (1922).—It was not found possible to duplicate the yield of 70-5% isostrychnine (*A*) claimed by Pictet (*Ber.* **38**, 2787) to be obtained by heating strychnine with H<sub>2</sub>O at 160-80°. In this way only a 25% yield was obtained. By using NH<sub>3</sub> in MeOH at 160° for 6 hrs. a 40-50% conversion was obtained. *A* crystals with 3H<sub>2</sub>O and m. 223° *in vacuo*. In H<sub>2</sub>O at 100° it is 0.7% sol. In EtOH, [α]<sub>D</sub> = 24.1°; in HOAc, -39.47°. With MeI it gives a cryst. compd. Oxidation with KMnO<sub>4</sub> gave no characteristic acids; so the isomerism can hardly be of the fumaric type.

O. B. HELFRICH

Bixin. J. HERZIG AND F. FALTIS. *Ann.* **431**, 40-70 (1923).—The results of the hydrogenation of bixin (*A*) and methylbixin (*B*) correspond best with the addn. of 18 H atoms. Hydromethylbixin (*C*) b<sub>18</sub> 280-5°. Hydrobixin is a viscous oil. Attempts to split the mol. of *C* resulted only in the sapon. of the MeO group, yielding hydronorbixin (*D*), b<sub>18</sub> 220-30° and behaves as a dibasic acid upon titration. With 3%, or with concd., MeOH-HCl it is changed into *C*. Heated at 320°, *D* is partially decompd. with the evolution of CO<sub>2</sub>. *Ca* salt of *C*, amorphous. Distd. with CaO at 11 mm. a product is obtained which analyzes for a mixt. of the hydrocarbon C<sub>28</sub>H<sub>46</sub> and the ketone C<sub>28</sub>H<sub>44</sub>O. No trace of *m*-C<sub>6</sub>H<sub>4</sub>Me<sub>2</sub> was found and it would appear that a certain degree of unsat. was necessary for the formation of this product. Oxidation with alk. KMnO<sub>4</sub> after sapon. gave an oil, C<sub>28</sub>H<sub>46</sub>O<sub>2</sub>, which yields a dimethyl deriv. with CH<sub>2</sub>N<sub>2</sub> or MeOH-HCl. *A* is not esterified either by 3% or concd. MeOH-HCl. The action of 3% MeOH-HCl upon *B* gives a β-methylbixin (*E*), m. 190-3°; this may be a new isomer. Very small amts. of this same deriv. are obtained by the action of CH<sub>2</sub>N<sub>2</sub> upon norbixin. β-Bixin has been isolated from Dutch annatto; it differs from *A* in its greater insoly. in AcOEt, in its Bordeaux-red color; it m. 211-4°, and upon methylation yields *E*, m. 188-9°.

C. J. WEST

The crystalline structure and properties of tartaric acid (ASTBURY) 2. Several optically active heavy metal complexes (LIFSCHITZ) 6.

BARRETT, W. H.: *Elementary Organic Chemistry*. Oxford: Clarendon Press; London: Oxford Univ. Press. 256 pp. 4s. 6d. Reviewed in *Nature* **111**, 321 (1923).

SCHMIDT, JULIUS: *Kurzes Lehrbuch der organ. Chemie.* 3rd Ed. revized. Stuttgart: F. Enke. 885 pp.

**Phthalimides.** H. D. GIBBS. U. S. 1,450,978, Apr. 3. A gaseous mixt. comprising  $C_6H_4$ ,  $O^2$  and an  $NH_2$ -contg. substance (e. g.,  $NH_3$ ,  $PhNH_2$ ,  $MeNH_2$ , or toluidine) is passed in contact with a catalyst such as oxide of V or Mo at a temp. of about  $400-500^\circ$  to form the corresponding phthalimides.

**Naphthylamines.** A. LOWY and A. M. HOWALD. U. S. 1,449,423, Mar. 27. Vapors of  $\beta$ -naphthol are subjected to the action of ammoniacal gases in the presence of  $Al_2O_3$  as a catalyzer at a temp. of  $300-550^\circ$ .

**Ketones from alkylsulfuric acids.** C. ELLIS and A. A. WELLS. U. S. 1,450,493, Apr. 3. Ketones which dissolve cellulose nitrate and acetate are prepd. by the action of  $H_2O$  and  $Na_2Cr_2O_7$  or other oxidizing agent on alkylsulfuric acids, e. g., those formed from cracked-oil gases and  $H_2SO_4$ .

**Naphthalene crystals.** D. F. GOULD. U. S. 1,448,688, Mar. 13. Crystals of  $C_{10}H_8$  in the form of aggregates are obtained by agitating a molten mass of  $C_{10}H_8$  with an aq. salt soln. which is immiscible with the  $C_{10}H_8$  and gradually cooling the mass during agitation to effect slow crystn.

**Purifying methanol.** W. ELSNER. U. S. 1,450,147, Mar. 27. MeOH contg. sulfurous impurities, dild. with about an equal amt. of  $H_2O$ , is treated with free Cl or other suitable chlorinating agent such as to furnish 7-8 parts of active Cl to 1 part S present, at ordinary temp.; the reaction is permitted to proceed for 12 hrs. and the mixt. is rectified.

**Separation of *o*- and *p*-nitroacetanilides.** KENKICHI MATSUO and the KÔRÔ SEIYAKU KABUSHIKI KAISHA. Japan. 40,523, Nov. 7, 1921. By the nitration of acetanilide, a mixt. of about 70% *p*- and 30% *o*- $O_2NC_6H_4NHAc$  is produced. Almost quant. sepn. is effected by dissolving the *o*-isomer in water at about  $80^\circ$ . The *p*-compd. has been considered to be decomposed by hot  $H_2O$  in the presence of an acid. M. has observed, however, that the compd. is stable, but the *o*-compd. is slightly decomposed into *o*-nitroaniline by treating with hot  $H_2O$  for a long time in the presence of an acid.

**Acetaldehyde from acetylene and steam.** DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT VORM. RÖSSLER. Ger. 334,357. In the prepn. of AcH by the interaction of  $C_2H_2$  and steam at high temp. in the presence of oxides or mixts. of oxides, the materials thus used as catalysts may become inactive. Their activity may be restored by the passage of a current of air, also at high temp. The effect of this treatment is either to oxidize C deposited on the catalyst or else to restore the partly reduced metallic oxides to their original state of oxidation. Large quantities of AcH may thus be prepd. from  $C_2H_2$  with only small quantities of catalyst. An example is given of the use as a catalyst of molybdic acid deposited on asbestos. J. C. S.

**Ethylidene diacetate.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE. Ger. 334,554. Ethylidene diacetate is prepd. by the action of  $C_2H_2$  on AcOH in the presence of Hg salts of aromatic or aliphatic sulfonic acids. The Hg sulfonates exhibit strong catalytic activity, and  $C_2H_2$  combines rapidly with AcOH at low temps. ( $40-65^\circ$ ). The Hg salts of benzenesulfonic, naphthalenesulfonic, and camphorsulfonic acids may be used but the Hg salts of aliphatic sulfonic acids are more satisfactory, e. g., those of sulfoacetic acid, acetaldehydedisulfonic acid, and methanedisulfonic acid. Examples are given of the use of Hg naphthalene- $\beta$ -sulfonate and Hg sulfoacetate. J. C. S.

**Hydantoin.** CHEMISCHE FABRIK VON FRIEDR. HEYDEN. Ger. 335,994; cf. Ger. 309,508, 310,426, 310,427. Alternatively to earlier methods of prepg. hydantoin, arylalkylmalonanitriles are treated with hypohalites. E. g., phenylethylmalonanitrile, b<sub>10</sub> 130-3°, prepd. from phenylethylcyanacetamide by distn. in a vacuum

with  $\text{PCl}_5$ , gives on treatment with  $\text{KBrO}$  soln. and subsequent warming *phenylethylhydantoin*. By alkylation of phenylcyanacetamide, *phenylisopropylcyanacetamide*, m.  $127^\circ$ , is obtained; this gives by distn. with  $\text{PCl}_5$ , *phenylisopropylmalononitrile*,  $b_{11}$   $143^\circ$ . From the latter *phenylisopropylhydantoin* is prepd., m.  $210-12^\circ$ . *Phenylbenzylmalononitrile*,  $b_{11}$   $194^\circ$ , m.  $97^\circ$ , gives similarly *phenylbenzylhydantoin*, m.  $209-10^\circ$ . *Phenylbenzylmalononitrile* is obtained from *phenylbenzylacetamide*, m.  $135^\circ$ .

J. C. S.

**Hydantoin.** CHEMISCHE FABRIK VON FRIDR. HEYDEN. Ger. 335,993; cf. Ger. 309,508, 310,426, 310,427.  $\text{NH}_3$  or monoalkylamines are allowed to react with urethanoaryalkylacetic esters of the general formula  $\text{CO}_2\text{R}.\text{NH}.\text{CR}''\text{R}'''.\text{CO}_2\text{R}'$ . Methyl  $\alpha$ -amino- $\alpha$ -phenylpropionate by reaction with methyl chloroformate and  $\text{Na}_2\text{CO}_3$  soln. gives methyl  $\alpha$ -urethano- $\alpha$ -phenylpropionate,  $\text{CO}_2\text{Me}.\text{NH}.\text{CMePh}.\text{CO}_2\text{Me}$ , colorless crystals, m.  $45^\circ$ . This when heated for 8 to 10 hrs. with alc.  $\text{NH}_3$ , gives after removal of alc. and  $\text{NH}_3$ , the residue being dissolved in dil.  $\text{NaOH}$  soln., and acidified, 5-phenyl-5-

methylhydantoin (I), colorless needles, m.  $193^\circ$ . (I)  $\text{CMePh} \begin{array}{c} \text{CO}-\text{NH} \\ | \\ \text{NH} \cdot \text{CO} \end{array}$  (11)

$\text{CEtPh} \begin{array}{c} \text{CO}-\text{NEt} \\ | \\ \text{NH} \cdot \text{CO} \end{array}$ . In a similar manner from ethyl urethano- $\alpha$ -phenylbutyrate,  $\text{CO}_2\text{Et}.\text{NH}.\text{CEtPh}.\text{CO}_2\text{Et}$ , a thick oil,  $b_{11}$   $186-8^\circ$ , and alc.  $\text{NH}_3$ , 5-phenyl-5-ethylhydantoin, is obtained, as colorless spikes, m.  $197^\circ$ . By heating the urethano- $\alpha$ -phenylbutyric ester with 35% monoethylamine soln. for 10 hrs., 5-phenyl-3,5-diethylhydantoin (II) is obtained, fine needles, m.  $88^\circ$ . By the action of  $\text{NH}_4\text{CN}$  on acetopiperone and hydrolysis,  $\alpha$ -amino- $\alpha$ -piperonylpropionic acid is obtained, which gives with  $\text{MeOH}$  and  $\text{HCl}$  the methyl ester, a colorless oil,  $b_{16}$   $193-4^\circ$ , from which by means of methyl chloroformate and  $\text{NaCO}_3$  soln. methyl  $\alpha$ -urethano- $\alpha$ -piperonylpropionate is obtained as colorless crystals, m.  $78-80^\circ$ . The latter by heating with alc.  $\text{NH}_3$  gives 5-piperonyl-5-methylhydantoin, colorless leaflets, m.  $192-4^\circ$ . By heating ethyl  $\alpha$ -urethano- $\alpha$ -p-chlorophenylbutyrate, a thick oil crystg. after a time in the cold with alc.  $\text{NH}_3$ , 5-p-chlorophenyl-5-ethylhydantoin is obtained, colorless needles, m.  $212^\circ$ . *p*-Chloropropiophenone when heated with  $\text{NH}_4\text{CN}$  gives  $\alpha$ -amino- $\alpha$ -chlorophenylbutyronitrile, which by hydrolysis with  $\text{HCl}$  gives  $\alpha$ -amino- $\alpha$ -chlorophenylbutyric acid. The Et ester of the latter gives the corresponding urethan by reaction with ethyl chloroformate in the presence of  $\text{H}_4\text{CO}_6$ .

J. C. S.

***N*-Substituted oxindoles.** ROBERT STOLLÉ. Ger. 335,673. *N*-Monohalogen acetyl derivs. of secondary alkylaryl- or diaryl-amines of the general formula  $\text{NRR}'.\text{CO}.\text{CH}_2\text{X}$  ( $\text{R}$  = alkyl or aryl,  $\text{R}'$  = aryl,  $\text{X}$  = halogen) are heated with Al halides. Ring formation, whereby the *N*-oxindole deriv. is formed, takes place with elimination of the corresponding H halide, the halogen atom of the acetyl group combining with the neighboring *o*-H atom of the benzene nucleus. *1-Ethyl oxindole* is obtained by heating chloroacetylphenylamide (from chloroacetyl chloride and ethylaniline in presence of alc., m. about  $35^\circ$ ,  $b_{11}$   $165^\circ$ ) with  $\text{AlCl}_3$  for 4 hrs. at about  $160^\circ$ ; it m.  $97^\circ$  after recrystg. from water or acetone. Chloroacetylphenylamide,  $\text{NPh}_2.\text{CO}.\text{CH}_2\text{Cl}$ , when heated with  $\text{AlCl}_3$  at  $160-70^\circ$  gives *1-phenyloxindole*, m.  $121^\circ$ . By the action of an oxidizing agent such as nitrosodimethylaniline, *diphenylisoindigotin*, m.  $315^\circ$ , is obtained. With bleaching powder, 3,3-dichloro-1-phenyloxindole is formed, m.  $118^\circ$ . When chloroacetylphenylamide (colorless needles, m.  $70^\circ$ ) is heated with  $\text{AlCl}_3$  at  $170-80^\circ$ , 1-methyl-oxindole is obtained, m.  $89^\circ$ . By the action on this of nitrosodimethylaniline or  $\text{NaIO}$ , dimethylisoindigotin is obtained, forming dark brown needles, m.  $265^\circ$ .  $\text{HNO}_2$  or amyl nitrite and Na ethoxide give with 1-methyloxindole, oximinomethyloxindole, forming yellow needles.

J. C. S.

**3-Nitroquinoline and its derivatives.** BADISCHE ANILIN- & SODA-FABRIK. Ger.

335,197. *o*-Amino derivs. of aromatic aldehydes or ketones or derivs. of these aldehydes or ketones are condensed with methazonic acid. 3-Nitroquinoline is obtained from *o*-aminobenzaldehyde and methazonic acid soln. after remaining for several hrs. at ordinary temps., and being acidified with HCl; it forms colorless crystals, m. 128°, easily volatile in steam. By the action of methazonic acid on an alk. soln. of isatin and acidifying with HCl,  $\beta$ -isatinoxime is obtained together with 3-nitroquinoline-4-carboxylic acid, which can be sepd. from the oxime by means of  $\text{NaHCO}_3$  and forms colorless needles, m. 204°. By treating *o*-aminoacetophenone, dissolved in water with the addn. of HCl, with methazonic acid soln. and acidifying with HCl, a mixt. is obtained of *o*-aminoacetophenoneoxime and 3-nitro-4-methylquinoline. These are sepd. by treatment with NaOH soln., in which only the oxime is sol. The nitro compound crystallizes from hot water in colorless prisms, m. 118°, volatile in steam. J. C. S.

Polycyclic hydrocarbons of the terpene series. CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING). Ger. 353,933. Hydrazones of terpene ketones are heated with HgO in indifferent solvents; or the double salts of the hydrazones with  $\text{HgCl}_2$  in the presence of an equiv. amt. of alkali are heated in indifferent solvents. Slightly sol. basic Hg compds. are thereby formed, which decompose on heating, as, for example,  $\text{C}_{10}\text{H}_{14}\text{N.NH.Hg.OH} = \text{C}_{10}\text{H}_{14} + \text{N}_2 + \text{Hg} + \text{H}_2\text{O}$ . Tricyclene, b. 153.5°, m. 63.5°, is formed from camphor hydrazone and HgO in alc. after 8 hrs.' heating. *d*-Cyclofenchene, from *d*-fenchone hydrazone, b. 142.5–3.5°,  $d_4^{20}$  0.8598,  $n_D^{20}$  1.45134,  $[\alpha]_D^{20} +0.45^\circ$ . Apocycene, from camphenil hydrazone, b. 138–139°,  $b_{17}$  120.5°, m. 40.1°,  $d_4^{16}$  0.8694,  $n_D^{45}$  1.44914. J. C. S.

New derivatives of the carbohydrates  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  and their homologs. LEON LILIENTHAL. Austrian 82,396. Etheral derivs. of the polyoses are prepd. by treating these substances in alk. soln. or basic derivs. such as their alk. earth,  $\text{NH}_4$ , Zn, Ag or Pb compds. with alkylating agents such as halogen-substituted alcs. or alkyl sulfates. The reaction proceeds in two stages. In the first stage ethers sol. in water are obtained. By further alkylation, ethers are obtained which are insol. in water. By the action of  $\text{EtI}$  or  $\text{Et}_2\text{SO}_4$  on starch in 10% NaOH soln., starch ethyl ethers are obtained which are distinguished by their soly. in water. The ether insol. in hot water forms a white, pulverulent or flocculent mass sol. in cold water. Another ether is insol. both in hot and cold water and forms a white powder. Tragacanth ethyl ether, similarly prepd., is a white or gray powder insol. in hot or cold water. Dextrin ethyl ether has similar properties. Inulin ethyl ether forms a viscous mass insol. in hot or cold water. The ethers are stable on heating and in the presence of acids and alkalies. Their solns. in org. solvents leave on evapn. transparent films which are chemically and physically resistant. J. C. S.

Complex silver compounds. F. HOFFMANN-LA ROCHE & Co. Ger. 350,912, Swiss 90,809, 91,108, 91,109; cf. Myers, C. A. 15, 2274. Org. or inorg. silver salts are allowed to react with thioacyl derivs. of aromatic amines.  $\alpha$ -Thiolacetamidophenol, an amorphous, yellow powder, m. 105°, from chloroacetamidophenol and Na persulfide, is allowed to react with  $\text{AgNO}_3$  soln. The silver  $\alpha$ -thiolacetamidophenol obtained contains 37.2% of Ag and gives no ppt. with  $\text{NaCl}$ ,  $\text{H}_2\text{S}$  or  $(\text{NH}_4)_2\text{S}$  solns. From sodium  $\alpha$ -thiolacetamidosalicylate, silver sodium  $\alpha$ -thiolacetamidosalicylate is obtained.  $\alpha$ -Thiolacetamidosalicylic acid, obtained from chloroacetamidosalicylic acid and Na persulfide, is a light yellow powder, m. 223°. It gives a sodium salt. Similar products are obtained by the action of  $\text{AgNO}_3$  on the Na salts of thiolisovaleramidosalicylic acid and thiolpropionamidosalicylic acid, resp. The latter compd. m. 226°. These acids are prepd. by the action of Na persulfide on bromoisovaleramidosalicylic acid and bromopropionamidosalicylic acid, resp. J. C. S.

Formyl derivatives of secondary bases. E. MERCK. Ger. 334,555. Formyl

derivs. of secondary bases are obtained by the action of chloral hydrate on the free bases. By the action of chloral hydrate on 2-methylomopiperonylmethylamine, with cooling, a *formyl* compd. is obtained. It m. 94-5°. From piperidine, *formylpiperidine* is obtained, as an oil,  $b_{17}$  106-10°. J. C. S.

**Nitro derivatives of  $\beta$ -azides of the anthraquinone series.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. Ger. 337,734.  $\beta$ -Azides of the anthraquinone series are treated with strong  $\text{HNO}_3$  or  $\text{HNO}_2$  and  $\text{H}_2\text{SO}_4$ . The nitro group enters the  $\alpha$ -position next to the azide group. 1-Nitro-2-azidoanthraquinone, prepd. by the action of fuming  $\text{HNO}_3$  on 2-azidoanthraquinone, forms yellowish green crystals becoming light orange-red on exposure to light and air, m. 210° (decompn.). On heating an aq. suspension with  $\text{Na}_2\text{S}$ , the color becomes green and then violet, and by further heating 1,2-diaminoanthraquinone crystallizes out with evolution of N. By addn. of 2,6-diazoanthraquinone to cold fuming  $\text{HNO}_3$  or a soln. of  $\text{KNO}_3$  in strong  $\text{H}_2\text{SO}_4$  with cooling, 1,5-dinitro-2,6-diazoanthraquinone seps. in yellow crystals which, after recrystn. from nitrobenzene, form light yellow needles, m. 200°; at 202°, sudden decompn. takes place with sepn. of C. Reduction with  $\text{Na}_2\text{S}$  gives 1,2,5,6-tetraminoanthraquinone. J. C. S.

**Fructosemonophosphoric acid.** FARBENFABRIKEN VORM. F. BAYER & CO. Ger. 334,250. Fructosediphosphoric acid or its salts are heated with dil. acids until one mol. of phosphoric acid is split off. E. g., the insol. Ca salt of fructosediphosphoric acid is changed into the Ca salt of fructosemonophosphoric acid,  $\text{CaH}_{11}\text{O}_5\cdot\text{PO}_4\text{Ca}\cdot\text{H}_2\text{O}$ , sol. in water but precipitable by  $\text{H}_2\text{O}$ . Fructosemonophosphoric acid, obtained from fructosediphosphoric acid, gives with phenylhydrazine an *osazone*,  $\text{C}_{22}\text{H}_{33}\text{O}_7\text{N}_6\text{P}$ , in large sheaves or druses, m. 153°. J. C. S.

**An  $\alpha$ - $\beta$ -tetrahydronaphtholcarboxylic acid and its ester and acyl derivative.** TETRALIN G. M. B. II. Ger. 357,663. An unhyd. alkali salt of  $\alpha$ - $\beta$ -tetrahydronaphthol is treated with  $\text{CO}_2$  at temps. above 100°. After acidification, the resulting product is changed into esters or acyl derivs. by the usual methods. The K salt of  $\alpha$ - $\beta$ -tetrahydronaphthol, freed from water in a stream of H at 150-160°, is treated with  $\text{CO}_2$  under pressure for several hrs. at 160-70°. After one mol. of  $\text{CO}_2$  has been absorbed, the product is dissolved in water and acidified with HCl. The  $\beta$ -tetrahydronaphthol- $\alpha$ -carboxylic acid thus obtained forms colorless needles, m. 177-8°. It gives a deep blue coloration with  $\text{FeCl}_3$ . The *methyl* ester  $b_{20}$  184-5°; it has an odor like that of Et acetoacetate, and forms a cryst. mass on keeping. By the action of  $\text{Ac}_2\text{O}$  on the carboxylic acid at 100° in the presence of  $\text{H}_2\text{SO}_4$ ,  $\beta$ -acetoxytetrahydronaphthalene- $\alpha$ -carboxylic acid, m. 142-3°, is obtained. J. C. S.

**Alkyl vinyl ethers and their homologs.** PLAUSONS FORSCHUNGSINSTITUT G. M. B. H. Ger. 338,281. See also Plauson and Vielle, C. A. 15, 1728. Homologs of alkyl vinyl ethers are prepd. by replacement of the  $\text{C}_2\text{H}_5$  group by homologous groups. *Ethyl vinyl ether*,  $b_{76}$  35°, is decomposed by  $\text{H}_2\text{SO}_4$ . J. C. S.

## 1—BIOLOGICAL CHEMISTRY

PAUL E. HOWE

A—GENERAL

FRANK P. UNDERHILL

**The anticatalytic action of hydrocyanic acid.** OTTO WARBURG. *Naturwissenschaften* 11, 159 (1923).—Based on the fact that traces of HCN inhibit the catalytic action of blood charcoal in oxidizing leucine and  $(\text{CO}_2\text{H})_2$ , it is suggested that the poisonous effect of HCN on the living cells is due to a similar action. Since HCN reacts with metals and since blood charcoal contains Fe, Cu, etc., expts. were made to prove

that the anticycatalytic action was due to a reaction with the metallic compds. present. Blood charcoal, after being heated in a sealed tube with HCl to ext. the metallic compds., was as active a catalyst in oxidation as the unextd. charcoal, and its catalytic action was far greater in the presence of HCN than the unextd. charcoal. The catalytic action of charcoal made from crystd. cane sugar, and free from metallic compds., was not inhibited by HCN. It is inferred that the smaller the % of heavy metals a charcoal contains, the less the anticycatalytic action of HCN. Since sugar charcoal contains no metals, its catalytic action cannot be due to these, but unlike blood charcoal, it adsorbs O in H<sub>2</sub>O suspension. Blood charcoal contg. 5% ash adsorbs O only after heating under pressure with HCl, indicating that the C is protected from adsorbing O by metallic salts, and only by their removal is the charcoal activated. C. C. DAVIS

**The ionic theory of the auditory adaptation.** P. P. LAZAREV. *Bull. acad. sci. Russie* 1919, 1055-1062.—The theory is proposed that mechanical resonance by acting upon the end points of the auditory nerves makes an intermediate phono-chemical reaction take place in a special substance located at the end points of the rods of Corti. Suppose that a sound has an intensity  $U$ , and develops in the rods of Corti vibrations of the intensity  $nU$ , which produce a phono-chemical process of the intensity  $mnU$ , this process being defined by a primary reaction velocity of  $\beta_1 mnUC$ , where  $C$  is the concn. of the phono-sensitive substance, and by a secondary phenomenon of a removal of the reaction products with a velocity proportional to their concn.  $B$  and to another const.  $\beta_2$ . If  $E$  is the momentary ear sensitivity produced after the sound acted upon it for a time  $\tau$ ,  $E = [\beta_1 mnC_0/B(\beta_1 mnU + \beta_2)] + [\beta_1^2 m^2 n^2 UC_0/\beta_2 B(\beta_1 mnU + \beta_2)] [e - (\beta_1 mnU + \beta_2)\tau]$ . If the energy of the sound  $U$  is const., the coeffs.  $m$  and  $n$  too become const. and the whole equation can be replaced by  $E = A + B e^{-R\tau}$  where  $A, B, R$  are empirical consts. In the case where the energy of the sound becomes very great and the auditory excitation lasts long enough,  $E$  becomes equal to  $C_0/B U = \text{const.}$  Supposing that long continued sounds of a great intensity practically destroy the phono-sensitive substance, which begins to form again, during the periods of silence, with a velocity proportional to  $\beta_3(C_0 - C)$ , the sensitivity of the ear after the time  $T$  of rest becomes  $E = (\beta_1 mnC_0/\beta_2 B)(1 - e^{-\beta_3 T})$ , whereas the max. sensitivity equals (according to Loeb)  $\beta_1 mnC_0/\beta_2 B$ , and their relationship is:  $E/E_{\text{max}} = 1 - e^{-\beta_3 T}$ . To test conclusions of the mathematical development one ear was allowed first to adapt itself to a sound of a const. number of vibrations but of different intensity and for different intervals of time, and after this its sensitivity was tested by sounds of a far lesser intensity. The three equations for  $E$ , (1) for strong sounds acting during intervals  $\tau$ , (2) for periods of silence of the duration  $T$ , and (3) for very strong sounds and of a very long duration (3 min.), gave figures coinciding fairly well with the expl. results.

M. S. KORSUNSKY

**Potential differences occurring in a Donnan equilibrium and the theory of colloidal behavior.** A. V. HILL. *Proc. Roy. Soc. (London)* 102A, 705-10(1923).—J. Loeb demonstrated that the Donnan membrane equil. involving the presence of an indiffusible ion is the basis of the colloidal properties of a protein soln. by showing that the p. d. observed experimentally between a protein and a non-protein soln. sep'd. by a membrane agrees exactly with that calcd. from the difference in  $\alpha_H$ . H. maintains that this equality is a necessary consequence of thermodynamical reasoning (an example of which is developed) and its proof is independent of any theory of the mechanism by which the p. d. is produced. I. NEWTON KUGELMASS

**The physico-chemical mechanism of cell respiration.** OTTO MEYERHOF. *Lancet* 1923, I, 322-5.—A review. E. R. LONG

**The distinctive properties of amylases of different origin.** J. EFFRONT. *Compt. rend. soc. belge biol.* 1922, 12-3; *Physiol. Abstracts* 7, 87.—Different amylases are classi-

fied as follows: soly. in water, soly. in a soln. of NaCl, soly. in starch paste, optimum temp. of reaction, relation between power of liquefaction and power of saccharification, action on achroodextrin, degree of resistance to the chem. action of the medium and degree of thermostability.

H. G.

The biochemical effect of light rays. G. DREYER. *Trans. Oxford Univ. Jun. Sc. Club* [3] 1922, No. 7, 212-5; *Physiol. Abstracts* 7, 202.—The effect of ultraviolet light on many proteins is very marked. Many albumins may be quantitatively pptd. by this means. Owing, however, to the increasing turbidity it is a tedious matter in practice, and the pptn. has to be repeated many times. Plant albumins or vitellins are very susceptible, as are most globulins.

H. G.

Hemocyanin. III. The absorption of light by oxyhemocyanin. G. QUAGLIARIELLO. *Publ. St. Zool. Napoli. Ric. fisiol. chim. biol.* 1, 57(1922); cf. *C. A.* 15, 3292.—Oxyhemocyanin from molluscs and arthropods shows one band in the yellow and the beginning of another in the blue. The former band is due to the Cu contained in an at. form in oxyhemocyanin, and corresponds with  $\lambda$  579  $\mu\mu$  in molluscs and  $\lambda$  563  $\mu\mu$  in arthropods. The second band corresponds with  $\lambda$  475  $\mu\mu$  in both types, and with the second band observed by Dhéré in the ultraviolet. Reduced hemocyanin does not form with K ferricyanide any compd. analogous to methemoglobin. J. C. S.

The reduction of methemoglobin by ammonium sulfide. G. QUAGLIARIELLO. *Arch. sci. biol.* 3, 308-12(1922).— $(\text{NH}_4)_2\text{S}$  reduces methemoglobin slowly in the cold, rapidly on warming, but without the formation of intermediate products. Oxyhemoglobin is formed after reduction has taken place if the solution is shaken. J. C. S.

Hemoglobin. II. The peroxidase content of blood. HSIEN WU. *J. Biochem. (Japan)* 2, 181-7(1923); cf. *C. A.* 17, 1041.—Blood contains no measurable amt. of a true peroxidase. The peroxidase activity of blood is practically the same as that of an equiv. quantity of hemoglobin which had been freed from all traces of peroxidase by the use of alumina cream in its prepn. A comparison of the peroxidase activity of hemoglobin and that of hemin shows that the former is about 1.38 times as active. Boiling the blood also reduces its peroxidase activity; for that of unboiled blood is 1.4 times as great as that of the boiled sample. IV. The catalase activity of hemoglobin and derivatives. *Ibid* 195-205.—The catalase activity is due to the hematin so that the Fe is evidently essential for both the catalase and peroxidase action of the hemoglobin. Hematin decomposes  $\text{H}_2\text{O}_2$  by catalysis and the  $\text{H}_2\text{O}_2$  decomposes hematin by oxidation. Thus on mixing a soln. of hematin with an excess of  $\text{H}_2\text{O}_2$  oxygen is evolved at the same time as the hematin is bleached. In an acid or neutral medium the catalase activity of hematin is very slight but increases with alk., reaching a max. when the concn. is about 0.187 N NaOH. Since expts. with 0.1 mg. hemin show a production of 5.7 cc. O. 1 cc. blood contg. 14% hemoglobin would yield 314 cc. O in 5 min. In neutral soln., however, the catalytic action is very much less and expts. with hemoglobin showed that this is still less active than hematin. In blood catalase expts. the error from this source would, therefore, not exceed 2%. Oxy-, carbonyl-, and met-hemoglobin are all about equally active, but hematoporphyrin is entirely inactive. This fact proves that the presence of Fe in the hemoglobin derivs. is responsible for their catalase action. S. MORGULNE

The lethal temperature of Koji-diastase in aqueous solution and the recovery of its action after heating. KOJI MIYAKE and MITSUJI ITO. *J. Biochem. (Japan)* 2, 255-70(1923).—It seems that the diastatic power of Koji-ext. injured by heating at a temp. lower than the lethal (140°) may recover its strength to some extent on preservation at room temp. The ext. heated at lethal temp. which lost its action completely never recovered its power of saccharification even by preservation for long intervals of time. The degree of recovery after heating increased with the prolongation of the

time for preservation of the ext. while it decreased with the increase of time of heating. However, it never attained a power equal to that of the original. Whether the recovery of diastatic action is due to the recovery of power of the enzyme weakened by heating or to the production of new enzyme from the mother substance present in the ext. is a problem which needs consideration. But it is assumed that the recovery is the restoration of activity of a weakened enzyme because the temp. at which the recovery ceases is the same as that at which the enzyme loses its activity. S. MORGULIS

**The inhibitory action of the salts of silver and some other heavy metals on amylase.** GENSICHI MORI. *J. Biochem. (Japan)* 2, 117-29(1922).—The amylase was freshly prepd. from barley. The measurements of the amylolytic activity were made as follows: to  $E$  cc. of the enzyme soln. was added  $A$  cc. of the soln. of the inhibitory substance, then 128 cc. of 2% sol. starch and  $H_2O$  to make the whole vol. 160 cc. The  $pH$  was adjusted with acetate-acetic acid mixt. to 5.6. 16 cc. of mixt. was removed every 10 min. and the maltose detd. by the methods of Bertrand, Mohr and of Fehling. The expts. were all made at  $30^\circ$ . Duclaux' rule expressed in the equation  $El/m = r$  (constant) holds closely until 35-40% starch is hydrolyzed. In this equation  $E =$  cc. enzyme;  $t =$  min.;  $m =$  % of starch hydrolyzed. Under the influence of an inhibitory substance the activity is diminished because of the decrease in active enzyme. The remaining enzyme is calcd. from the equation  $\epsilon = rm/t$ , where  $\epsilon$  is the enzyme residue. The enzyme is not actually destroyed but merely inhibited and can be again recovered. In the most dil. soln. of the  $AgNO_3$  employed the salt was present in a concn. of  $1.25 \times 10^{-3}$  mol., yet the activity of the enzyme was diminished 14%. The relation between the cc. of enzyme used and those remaining active is shown in curves. The inhibition may be due to an adsorption of the  $Ag$  salt or ion, and where the value of  $A$  is large  $\epsilon$  is directly proportional to  $E^1$  and inversely to  $A^1$ , i. e.,  $\epsilon = KE^1/A^1$ . This formula is also deduced from the assumption that the reaction follows the equation  $Z_1 + 2Ag = 2ZAg$ , where  $Z$  is the enzyme. The value of  $K$  was found by trial to be  $= 1/1.2$  and the calcd. data agree very well with the exptl. results. From these considerations M. calcs. the concn. of the enzyme as  $0.8 \times 10^{-8}$ , and assumes the mol. wt. of this to be 20000. A l. of the soln. would thus contain only  $1/3$  mg. of enzyme. That the  $Ag$  salt does not actually destroy the enzyme is shown by the fact that the addition of a single drop of  $H_2S$  causes a recovery of about 88% of the amylolytic activity. Besides the expts. with  $AgNO_3$ , the inhibitory action of  $AgCl$ ,  $AgBr$ ,  $NaAuCl_4$ ,  $CuSO_4$ , and  $Pb$  acetate was studied. In all cases the inhibitory action is a function of the concn. of the metal. The inhibitory effect of the salts of  $Ag$ ,  $Au$ ,  $Cu$  and  $Pb$  stands in the ratio of 1:1/18:1/30:1/1400. S. MORGULIS

**The absorption of alkalis, organic acids and of enzymes by vegetable pulp.** JEAN EFFRONT. *Compt. rend. soc. biol.* 83, 129-32(1923).—Vegetable pulp absorbs acids and bases, but it absorbs and holds in combination the latter with much greater vigor. The greater the concn. of the acid the less relatively it is adsorbed. The reverse is true for pepsin, the relative amt. absorbed increasing with the enzyme concn. S. M.

**Influence of vegetable pulp on the chemical conditions of the medium and on the coordination of the work of biochemical catalyzers.** JEAN EFFRONT. *Compt. rend. soc. biol.* 83, 132-5(1923).—3-5 g. of vegetable pulp can absorb 100 cc. water; most of this can be removed by pressure but a certain fraction remains firmly combined with the pulp. This fact has been utilized in bringing about concn. of various substances adsorbed by the pulp. A study of the differential adsorption of acid and of pepsin, and changes in reaction which could be made in these mixts. (details must be examd. in the original) lead to the conclusion that variations in enzymic activity and in the reaction of the internal medium which characterize the living processes of cells may be explained on the basis of the adsorption properties of colloids. S. MORGULIS



**Autolysis.** SHIN SHIMA. *J. Biochem. (Japan)* 2, 1-26(1922).—For liver autolysis there are 4 optimum H-ion concns.: at  $p_H = 3.24$ , which is probably the acidity at which the protease acts best; at  $p_H = 7.29$ , which is the optimal acidity for peptase; and  $p_H$  4.44 and 6.55, at which both enzymes apparently act simultaneously. Both protease and peptase are the enzymes concerned in the autolysis of liver. The passing of  $CO_2$  gas through the digest mixt. makes it slightly acidic and thus accelerates the autolysis, while O and H drive out the volatile acids formed during autolysis and by thus decreasing the acidity tend to inhibit the autolysis. NaCl in very dil. soln. is almost indifferent while in more concd. soln. ( $M/32$  and higher) it inhibits autolysis. KCl inhibited the liver autolysis at concns. as low as  $M/64$ .  $MgCl_2$  and  $BaCl_2$  both inhibited liver autolysis in all concns.  $CaCl_2$  accelerated the liver autolysis in fairly concd. soln.  $AlCl_3$  accelerated the autolysis exceedingly. In view of the fact that the  $AlCl_3$  solns. had a  $p_H$  range of 3.4 to 4.2 these expts. were controlled with HCl solns. of similar  $p_H$  value. The acceleration produced by the  $AlCl_3$  was then seen to be largely independent of the acidity.  $Na_2SO_4$  in dil. soln. always accelerated the autolysis. Dil. Na citrate accelerated the liver autolysis so far as the non-coagulable N was concerned but not the amino N. The same effect was also produced with  $Na_4Fe(CN)_6$ , in which case the amino-acid N was already much reduced by very dil. solns. Although it seems strange that multivalent anions and cations which usually act antagonistically to each other both accelerate the liver autolysis, this is not inconsistent when the existence of 2 enzymes is assumed. The active pepsin has as cation a positive charge and the optimal digestion of pepsin is in an acid medium. In the acid soln., however, the protein also takes a partly positive charge, as the positively charged active pepsin can hardly unite with the positively charged protein ion. It is probable, therefore, that the pepsin digests the protein after uniting with the non-dissociated protein mol. The added multivalent anion may give a negative charge to the non-dissociated protein mol. and lets the union of the latter and the positively charged pepsin take place easily, and thus accelerates the digestion in autolysis. On the other hand, the active erepsin has a negative charge and since in an alk. medium part of the protein is negatively charged, it seems reasonable to assume that the erepsin digests the protein after uniting with the non-dissociated protein mol., and this phenomenon is assisted by the added multivalent cations which charge the non-dissociated protein mol. positively. This explanation of the mechanism of the action of proteolysis is corroborated by the expts. showing the influence of Na citrate and  $Na_4Fe(CN)_6$ ; namely, that the increase of non-coagulable N is found at the concn. of these salts at which the production of the amino-acid N decreases, indicating that in this concn. they promote the peptic digestion but inhibit the ereptic activity. Furthermore, it is known that  $Na_2SO_4$  and  $MgSO_4$  accelerate peptic digestion while the halogen salts of Ca and Mg inhibit it, and that the  $SO_4$  ion inhibits tryptic action, all of which observations coincide with the results obtained in the autolysis expts. with liver. Mg and Ba ions are supposed to act poisonously on the enzymes and thus inhibit autolysis. From these expts S. concludes that there are at least 2 enzymes in the tissues concerned with autolysis.

S. MORGULIS

**The adsorption of sodium salicylate by blood serum.** II. CHABANIER, M. LEBERT, AND C. LOBBO-ONELL. *Compt. rend. soc. biol.* 88, 178-80(1923).—By means of dialysis expts., in which serum to which a definite amt. of Na salicylate was added was dialyzed against an isotonic salt soln. contg. exactly the same concn. of the salicylate, it was shown that the serum adsorbed the salicylate from the outside soln. No account was taken of the  $p_H$  values.

S. MORGULIS

**Pancreatic hormone as an activator of certain muscular enzymes.** EYVIND ROSLING. *Compt. rend. soc. biol.* 88, 112-4(1923).—Procedure: 0.3 g. of muscle finely

ground and well washed with water is mixed with 0.2 cc. of a 1:5000 methylene blue soln., 0.2 cc. buffer mixt. (6.6 g.  $K_2HPO_4$  + 1.6 g.  $KH_2PO_4$ ), and 0.2 cc. 0.1 N of either  $\beta$ -hydroxybutyric or glutamic acid. To this is added pancreatic ext. and the vol. made up to 1 cc. The tubes are incubated at 40°, and from the time necessary to bring about complete decolorization of the methylene blue (0.04 mg.), the reduction per 100 min. is detd. The reduction takes place only in the presence of pancreatic ext. The substance which is responsible for this activation of the muscle enzymes is dialyzable and is not destroyed by boiling in an acid medium. S. MORGULIS

The reaction of the musculature of different animals with *d*-tartaric and with *l*-tartaric acids. JÖRGEN LEHMANN. *Skand. Arch. Physiol.* 42, 266-72(1922).—Thunberg discovered that finely cut muscle washed with  $H_2O$  until it failed to decolorize methylene blue can be reactivated by *l*-tartaric acid, suggesting the possibility that this is an intermediate product in muscle metabolism. The study has been extended to a large variety of animals. The dehydrogenase activity was calcd. from the formula  $I = 100[(1/A) - (1/B)]$ , in which *A* is the time required for decolorization in the presence of a donor and *B* without any donor. The reaction with both antipodes of tartaric acid was then detd. from the ratio *I*:*I*<sub>0</sub>. If the ratio is greater than 1, the musculature is more activated by *l*- than by *d*-tartaric acid. The results of expts. performed with a number of invertebrates and vertebrates agree with those of Thunberg, only in the case of rabbit and ox muscle, the activation by both the *l*- and *d*-acid being about the same. The expts. suggest that there are possibly different enzymes concerned with the dehydrogenation of the *l*- and *d*-acid, the latter being the less stable or more easily extd. from the muscle substance. The optimum H-ion concn. is also different for the 2 enzymes: for the *l*-tartaric acid the more alk. the reaction of the medium the sooner did decolorization occur, while the greatest rate of activity for the *d*-tartaric acid was found in a practically neutral medium. The *d*-tartaric enzyme also showed itself more resistant to temp. extremes than the *l*-tartaric. S. MORGULIS

An experimental investigation of the chemical process involved in the taste reaction with hydrogen peroxide. YRJÖ RENQVIST. *Skand. Arch. Physiol.* 42, 272-80(1922).—The stimulation of the sense of taste by  $H_2O_2$  is considered to be a chem. process.

S. MORGULIS

The coagulation of albumin by alcohol and other organic substances. V. V. LEPESHKIN. *Kolloid Z.* 32, 100-3(1923); cf. *C. A.* 17, 405.—Adding alc. to albumin solns. produces first "denaturation" and then an insol. ppt. At higher temps. the insol. ppt. forms in much shorter time than at lower. The process is reversible and very similar to the coagulation produced by salts. Alc. addn. results in a distribution of water between the alc. and the albumin, and hence dehydration of the albumin. Non-sol. substances like  $Et_2O$ ,  $CHCl_3$ ,  $C_6H_6$  and chloral hydrate which form colloidal solns. in water denaturalize or coagulate but do not form an insol. ppt. of albumin on the surface of the dispersed fluid particles. A. MÜTSCHALLER

Membrane potentials and the cataphoretic potentials of proteins. JACQUES LOEB. *J. Gen. Physiol.* 5, 505-19(1923).—Membrane potentials of protein solns. or gels are detd. by differences in concn. of a common ion (H ion) inside a protein soln. or gel and an outside aq. soln. free from protein. On the basis of the Helmholtz theory of elec. double layers, it is assumed that the cataphoretic potentials of protein solns. are detd. by the difference in concn. of 2 oppositely charged ions of the same electrolyte in the 2 strata of an elec. double layer surrounding the protein particle and situated entirely in the aq. soln. Membrane p. ds. and cataphoretic p. ds. agree in that the charge on the protein is negative on the alk., and positive on the acid, side of the isoelec. point of the protein. The 2 types of p. ds. disagree in regard to the action of salts with trivalent and quadrivalent ions on the sign of the charge on the protein. Low concns.

of these salts reverse the sign of the cataphoretic p. d. of the protein particle, but bring the membrane p. d. to zero. The cataphoretic migration and the cataphoretic p. d. of protein particles or suspended particles coated with protein are the result of forces inherent in the protein particles (and linked with the membrane equil.) and forces inherent entirely in the aq. soln. The cataphoretic migration of protein particles is detd. by the forces resulting from the membrane equil. and hence related to the forces inherent in the particles themselves.

CHAS. H. RICHARDSON

The selective absorption of potassium by animal cells. III. The effect of hydrogen-ion concentration upon the retention of potassium. R. B. STANTON. *J. Gen. Physiol.* 5, 461-8(1923).—*Rana catesbiana* was perfused with a soln. contg. 6.7 g. NaCl and 0.25 g.  $\text{CaCl}_2$  per l., adjusted to various  $p_{\text{H}}$  with 1%  $\text{Na}_2\text{CO}_3$  soln. Analyses of the gastrocnemius muscle showed that with perfusion periods of 30 min. to 16 hrs. and  $p_{\text{H}}$  6.0 to 8.0, no effect was produced upon the retention of K by the muscle cells. The solids of the fresh muscle of male frogs had 1.874% K or 4.26% more than that of females. The fresh, moist muscle held an av. of 0.343% K for both sexes. The muscles were alive after these perfusion tests.

CHAS. H. RICHARDSON

Stability of suspensions of solid particles of proteins and protective action of colloids. JACQUES LOEB. *J. Gen. Physiol.* 5, 479-504(1923).—The concns. of salts required to ppt. aq. suspensions of colloid particles coated with gelatin are about equal to the concns. required for the "salting out" of gelatin from aq. solns. These effects show no relation to the elec. double layers surrounding the particles. At the isoelec. point of gelatin, suspensions of these gelatin-coated particles are not stable. The addn. of salt increases the soly. of gelatin in  $\text{H}_2\text{O}$  and the stability of the gelatin-coated particles. Both effects increase with the valency of one of the ions of the salt; but cataphoretic expts. showed that the increase in stability was not due to elec. charges conferred by the salts. These facts indicate that the stability of aq. suspensions of these gelatin-coated particles depends on the soly. of the gelatin in  $\text{H}_2\text{O}$ , *e. g.*, on the chem. affinity of certain groups of the gelatin mol. for  $\text{H}_2\text{O}$ . Colloid particles coated with cryst. egg albumin depend for their stability almost entirely on the elec. double layer surrounding the particles. When the p. d. of this layer falls below 13 milliv., the suspension is no longer stable. The crit. p. ds. for the stability of colloid particles coated with genuine egg albumin and of particles of denatured (boiled) egg white are identical. By the heating process, egg albumin loses its soly. in  $\text{H}_2\text{O}$ ; probably it undergoes the same change upon forming a film around a colloid particle. The stability of colloid particles coated with casein or edestin is similarly influenced by salts. However, their behavior toward NaCl and  $\text{CaCl}_2$  solns. was anomalous, probably because of soly. phenomena. Protective colloids must be able to form a durable film on the surface of suspended particles and the mols. of this film must have a higher attraction for the solvent mols. than for each other, *e. g.*, they must possess true soly. Particles kept in suspension by the high p. d. of an elec. double layer are pptd. by low concns. of electrolytes.

CHAS. H. RICHARDSON

Autoxidation. Cysteine and tissues. Hydrocyanic acid intoxication. E. M. ABERKHALDEN and ERNST WERTHEIMER. *Arch. ges. Physiol.* (Pflüger's) 197, 131-46 (1922).—Cysteine, or cysteine-contg. compds., is present in all living cells, suggesting a very great importance to this autoxidizable substance. The sulphydryl group of cysteine is spontaneously oxidized and is again reduced by the tissues. The reaction optimum for this process is in accord with the reaction of the body fluids. The autoxidation is favored by Fe, Cu, Hg, and As; it is inhibited by Pb, Ni, Co, U, Th, and Cd. Light is without effect. Alcs.,  $\text{CHCl}_3$  and  $\text{Et}_2\text{O}$  accelerate the reaction. Boiling quickly oxidized the sulphydryl group. The thio group of cysteine offers the point of combination for KCN or HCN, and this is concerned in the inhibition of the autoxidation by HCN.

The addition of traces of ferric chloride prevents this inhibitory action, as do  $\text{Et}_2\text{O}$  and the higher alcs. G. H. SMITH

**Action of hormones on cellular oxidations and on the heat regulation of the organism.** LEO ADLER AND WERNER LIPSCHITZ. *Arch. exp. Path. Pharm.* 95, 181-91 (1922).—One of the actions of hormones is a considerable effect upon the oxidation velocity of isolated muscle cells, involving metabolism and heat regulation. The nitro-reduction method serves very well for evaluating the metabolic activities induced by hormones, and supplements the tadpole metamorphosis method. Thus, by the reduction method, the respiration velocity of muscle cells was increased by 30 to 90% by thyroid, by 70% by adrenal, by 50% by epiphysis, by 30 to 150% by tyramine (0.025-0.5%), and by 30 to 50% by adrenaline (0.01-0.1%). Adrenal tissue in which there was an adenoma of the cortex caused an inhibition, as did pancreas from hibernating hedgehogs and thymus tissue. The pancreatic ext. and the tumor-adrenal tissue ext. caused a reduction in temp. when injected into rabbits. G. H. SMITH

**The propelling force for the fluid stream in the organism.** III. Permeability of the capillaries for protein. HERMUTH FREUND. *Arch. exp. Path. Pharm.* 95, 206-34 (1922).—Perfusion of the hind legs of frogs showed that the surviving normal capillaries are impermeable to protein, or if any passes through it is in such small amts. that it cannot be detected. In As intoxication of frogs the capillaries sometimes become permeable, protein passing in both directions, from blood to tissue or from tissue to blood. Perfusion of the extremities of normal frogs with hypertonic salt or crystalloid solns. and later with serum shows that the vessels have become permeable. The effect is still more manifest if the serum itself is made hypertonic. It is assumed that under these exptl. conditions the capillaries are killed, and that protein permeability is a property of dead capillaries. G. H. SMITH

**Does the taste of a salt depend upon the tastes of the individual ions or upon the entire molecule?** H. KIONKA AND F. STRÄTZ. *Arch. exp. Path. Pharm.* 95, 241-57 (1922).—Of 18 salts tested only one,  $\text{NaCl}$ , has a purely salty taste; the others have mixed tastes, usually combinations of salty with bitter. The taste quality of each salt changed with the concn. used. The relative roles of the anions and cations of the 18 salts, used in 0.1 *N* concns., showed that as regards the salty and bitter tastes the salts could be placed in 3 groups: (1) those with a dominating salty taste ( $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{NaBr}$ ,  $\text{NH}_4\text{Br}$ ,  $\text{LiBr}$ ,  $\text{NaI}$ ,  $\text{LiI}$ ); (2) those which were both salty and bitter ( $\text{KBr}$ ,  $\text{NH}_4\text{I}$ ); and (3) those characterized by the bitter taste ( $\text{CsCl}$ ,  $\text{RbBr}$ ,  $\text{CsBr}$ ,  $\text{KI}$ ,  $\text{RbI}$ ,  $\text{CsI}$ ). In general, salts with the  $\text{Cl}$  ion were outspokenly salty ( $\text{CsCl}$  being the exception). Of the 6 I salts 3 were bitter, 2 salty, and one had both properties. When arranged according to mol. wt. 3 groups were also evident; the 4 salts with the highest mol. wt. ( $\text{RbI}$ ,  $\text{CsI}$ ,  $\text{KI}$ ,  $\text{RbBr}$ ) were decidedly bitter. The next group of salts, i. e., those of the intermediate mol. wts., had both taste qualities. The 8 salts with the lowest mol. wts. had the predominant salty taste. (Again  $\text{CsCl}$  forms an exception.) Apparently the taste quality of a salt is dependent upon the cation which det. the intensity, and upon the anion which gives the character. The addition of colloids, sol. starch, had but little effect upon the taste. G. H. SMITH

**Influence of water on the electromotive properties of living tissue.** D. S. WORONOFF. *Arch. ges. Physiol. (Pflüger's)* 197, 471-81 (1923).—Potential detms. made upon the muscle tissue of frog, toad, and lizard when under the influence of water show that the rest current of muscle is materially smaller than that of normal tissue. When the tissue is treated with sugar soln. the rest current is much greater than that of normal tissue. *Lacerta viridis* muscle reacted exactly as frog muscle. Toad muscle differed materially in its action from that of frog tissue. G. H. SMITH

Equilibrated fluid of physiological hydrogen-ion concentration, capable of steril-

ization. ALFRED FLEISCH. *Arch. expil. Path. Pharm.* **94**, 22-7(1922).—The soln. has a  $p_H$  of 7.52 and this value is unchanged by standing or by heating for sterilization. The formula is: NaCl 10.5 g., KCl 0.5 g.,  $CaCl_2$  0.3 g.,  $MgCl_2$  0.1 g.,  $N H_2PO_4$  5 cc., water 50 cc. For use 50 cc. of the above soln. is added to 1000 cc. of water, filtered, sterilized, cooled, satd. with  $O_2$ , and mixed with 5 cc. of sterile  $N Na_2CO_3$  soln.  
G. H. SMITH

Solubility of uric acid in water. HEINRICH BILTZ AND LISBET HERRMANN. *Ann.* **431**, 104-11(1923).—His and Paul (*Z. physiol. Chem.* **31**, 1(1900)) reported the soly. of uric acid at  $18^\circ$  as 0.0253 g. per l. of  $H_2O$ . Because of the tendency to form supersatd. solns., when a hot soln. is cooled to  $14^\circ$  and allowed to stand 3-4 hrs., the soly. is found to vary between 0.07 and 0.0777 g. per l. The av. of 7 expts. gave a soly. of 0.0223 g. per l. when the acid was shaken with  $H_2O$  at  $14^\circ$  for periods of 1.5 to 24 hrs. If after cooling a hot soln., the mixt. is shaken for 18 hrs., the soly. is found to be 0.0308 g. per l., after 36 hrs., 0.0283 g. per l. This variation is of course due to the slow rate at which the supersatn. disappears. That uric acid is fairly stable is seen from the following: A 0.004 mol. soln. with a  $p_H$  of 4.64 was evapd. to dryness and again taken up in  $H_2O$ , when it showed a  $p_H$  of 4.70. A soln. of 3,9-dimethyluric acid with  $p_H$  5.52 showed a value of 5.58 after standing 2 months.  
C. J. WEST

Adsorption and detoxication power of certain charcoals (JOACHIMOGLU) 2.

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## B—METHODS AND APPARATUS

STANLEY R. BENEDICT

The determination of alkali in water and nutrient bouillon. H. NOLL. *Z. Hyg. Infektionskrankh.* **96**, 172-90(1922).—Titration of alk. of water, using Me orange directly or, after removal of  $CO_2$ , phenolphthalein or azolitmin, was found to be satisfactory. Fe, silicates and humin influence the accuracy of the titration, giving high results. For turbid solns., as bouillons, where phenolphthalein cannot be used, spotting on litmus paper was a suitable indicator.  
F. A. CAJORI

Histochemical detection of potassium. JOSEF KISSER. *Pharm. Presse* **28**, No. 5, 2-3(1923).—On an object glass moisten the plant section with a drop of Behrens' reagent ( $NaNO_2$  20 g.,  $Cu(OAc)_2$  9.1 g.,  $Pb(OAc)_2$  16.2 g. in 75 cc.  $H_2O$ , 75 cc. EtOH and 2 cc. AcOH), whereupon a ppt. of deep black, sharply defined cubes or plates of  $K_2CuPb_3(NO_3)_{14}$  almost immediately results.  
W. O. H.

Histochemical detection of calcium. JOSEF KISSER. *Pharm. Presse* **28**, No. 4, 2-3(1923).—Ca salts are detected in plants by treating with a drop of alc.  $H_2SO_4$  (30 cc. EtOH and 10 to 15 drops of concd.  $H_2SO_4$ ), whereupon acicular or dendritic cryst. clusters will almost immediately appear. Instead of alcohol, AcOH may be used

The method for the determination of the liquefying power of amylase. J. EFFRONT. *Compt. rend. soc. belge biol.* 1922, 7-9; *Physiol. Abstracts* 7, 87.—A new method is given based on the coagulating action of I on starch paste. This method is very rapid and is adapted to the study of bacterial cultures of the saliva and of the urine. H. G.

Colorimetric method for determining cystine. E. HERZFELD. *Schweiz. med. Wochschr.* 52, 411-2(1922); *Physiol. Abstracts* 7, 212. H. G.

Value of the method of Vastarini-Cresi in the histochemical detection of glycogen. A. POLICARD AND R. NOEL. *Compt. rend. soc. biol.* 86, 118-9(1922); *Physiol. Abstracts* 7, 83.—Vastarini-Cresi has described a method of staining glycogen in the liver with warm cresofuchsin in such a manner that during the necessary manipulations all water is rigidly excluded. Thus the whole of the glycogen is retained and the amt. present can be estd. from the depth of the staining. The authors have confirmed the truth of this by staining the livers of mice in the manner indicated and directly estg. the glycogen present nephelometrically. H. G.

Determination of hippuric acid in urine. I. SNAPPER AND E. LAQUEUR. *Arch. néerland. physiol.* 6, 48-57(1921); *Physiol. Abstracts* 7, 83.—The soly. of hippuric acid in AcOEt is utilized to sep. it from urine. Urea, which also dissolves, is decompd. by treatment with Br water; the N of the solute is then estd. (Kjeldahl) and the results are calcd. from this. H. G.

The determination of protein in urine. PAUL KAUFMANN. *Deut. med. Wochschr.* 49, 190(1923).—Treat 10 cc. of clear, acidified urine, in a test-tube, with 1 cc. of formalin. Mix the liquid thoroughly, stopper the tube, and set aside for 24 hrs. Traces of protein give a cloudy liquid; larger amts. lead to the formation of a sticky coagulum; large amts. of albumin may lead to the formation of a jelly-like mass. The first cloudiness may appear after 15 to 30 min.; but a test should not be termed negative unless the liquid remains clear for 24 hrs. MILTON HANKE

Several clinico-chemical methods. H. CITRON. *Klin. Wochschr.* 1, 2578-9 (1922).—The methods are gasometric. The detns. are carried out in a special app. (volumeter) which is not described in detail. The estn. of urea, in blood and serum, depends upon its reaction with NaOBr to give N. The vol. content of the food-free stomach is estd. as follows: The subject drinks 100 cc. of a 2% urea soln. The contents of the stomach are removed as soon as possible (stomach tube) and the concn. of urea in the extd. fluid is estd. From this figure the diln. of the urea soln. and the vol. of liquid originally present in the stomach are easily calcd. For the estn. of acetone in urine, a steam distn. is conducted in a special app. called a vaporizer. The vapors are collected in a soln. contg. 2 g. PhNHNH<sub>2</sub>.HCl and 20 g. NaOAc in 100 cc. of H<sub>2</sub>O. The concn. of unchanged PhNHNH<sub>2</sub> is detd. by mixing the reaction liquid with a soln. of CuSO<sub>4</sub> in the volumeter. N is evolved quant. from PhNHNH<sub>2</sub>, but not from the phenylhydrazone. MILTON HANKE

The purification of yeast invertase. KARL JOSEPHSON. *Arkiv. Kemi. Mineral. Geol.* 8, No. 26, 21 pp.(1923).—J. prepd. pure invertase by (1) autolysis of the yeast, (2) pptn. of the autolyzed liquor with alc., (3) adsorption by Al(OH)<sub>3</sub>, subsequent soln. and dialysis, (4) adsorption on kaolin, subsequent soln. and dialysis, (5) repetition of treatment (3). By this combination of methods previously utilized separately he achieved a much more rapid and thorough purification of the enzyme. Detailed tables demonstrate the increased strength of the invertase soln. after each successive purification; the bibliographical citations are not extensive. T. SWANN HARDING

Inhibition phenomena in amylases. URBAN OLSSON. *Z. physiol. Chem.* 119, 1-3(1922); cf. *C. A.* 16, 3495.—A method for measuring the liquefaction of starch is based on the principle of recording the time taken by a glass ball to drop in the starch soln. contained in an evacuated tube. J. C. S.

A gasometric method for the determination of urea nitrogen in the blood. A. MIRKIN. *J. Lab. Clin. Med.* **8**, 50-52(1922).—Urea is converted into  $(\text{NH}_4)_2\text{CO}_3$  by the action of urease, and the  $\text{CO}_2$  detd. in Van Slyke's app. From this the urea is calcd. Incubate 2 cc. plasma and 1 cc. urease soln. 10 min. at 45-50°. Run 1.5 cc. of this mixt. into Van Slyke's app., add 0.5 cc. distd. water and det. the  $\text{CO}_2$  (total) in the usual way. Incubate 2 cc. plasma and 1 cc.  $\text{H}_2\text{O}$  similarly and det. the  $\text{CO}_2$  (preformed). Calc. the urea present from the formula  $U_{100} = 63.6(V_1 - V_2)W_{24}$ , where  $V_1$  is the total  $\text{CO}_2$ ,  $V_2$  the preformed  $\text{CO}_2$ , and  $W_{24}$  the wt. of 1 cc. of  $\text{CO}_2$  at the temp. and pressure prevailing at the test. The wts. of  $\text{CO}_2$  at different temps. and pressures are taken from Van Nostrand's Chemical Annual (1919, p. 100). The figure 63.6 is obtained as follows:  $(\text{CO}(\text{NH}_2)_2/\text{CO}_2)(\text{N}_2/\text{CO}(\text{NH}_2)_2) \times 100 = 63.6$ .  $U_{100}$  is the amt. of urea in 100 cc. blood.

E. R. LONG

A new method for the determination of calcium, magnesium, potassium and sodium in human blood. A. MIRKIN AND S. J. DRUSKIN. *J. Lab. Clin. Med.* **8**, 334-9(1923).—Citratd blood is oxidized by heating with a mixt. of fuming  $\text{HNO}_3$  and concd.  $\text{H}_2\text{SO}_4$ . After evapn. a little  $\text{NH}_4\text{HCO}_3$  is added, volatile  $(\text{NH}_4)_2\text{SO}_4$  being formed. From this the  $\text{NH}_3$  can be detd. In the residue Ca and Mg are pptd. by  $\text{NH}_4$  stearate soln. and weighed as stearates. These are dissolved in 0.01 N  $\text{H}_2\text{SO}_4$ , the pptd. stearic acid is filtered off and the excess  $\text{H}_2\text{SO}_4$  titrated with 0.01 N NaOH. The total amt. of stearate and that of the stearic acid contained in both of them being known, the respective amts. of Ca and Mg can be calcd. The filtrate from the pptd. stearate is cvapd. to dryness and the residue heated to destroy  $\text{NH}_4$  stearate. After removal of the latter the residue consists of the alkali sulfates. From the amt. of  $\text{H}_2\text{SO}_4$  present the proportions of Na and K present can be calcd.

E. R. LONG

A modification of the Folin-Wu blood sugar method. SERGIUS MORGULIS, A. C. EDWARDS AND ELIZABETH A. LEGGETT. *J. Lab. Clin. Med.* **8**, 339-41(1923).—Blood filtrates are prepd. by the usual Folin-Wu method and 1 or 2 cc. boiled with alk.  $\text{CuSO}_4$  as usual. To each tube is added 1 cc. of Benedict's arsenotungstate soln. (uric acid reagent) modified by the addition of 8 cc. concd. HCl per 100 cc. This acid soln. dissolves the  $\text{Cu}_2\text{O}$  readily. The tubes are submerged in cold water 3 min., 1 cc. 10% NaOH is added and the contents of the tube are dild. with  $\text{H}_2\text{O}$  after 5 min. The color is matched with a standard. The uric acid of the blood does not interfere with the sugar reaction. Close checks with analyses by the Folin-Wu method were obtained.

E. R. LONG

Loss of sugar in oxalated blood. DORA E. BIRCHARD. *J. Lab. Clin. Med.* **8**, 346-9(1923).—The sugar content of oxalated blood decreases with a fair degree of regularity, approx. as follows: about 12% in the first 3 hrs., 22% in the first 6 hrs., and 32% in the first 24 hrs. The protein-free filtrate maintains a practically const. sugar content for at least 36 hrs. if kept on ice, or with the addition of a few drops of xylene if kept at room temp.

E. R. LONG

Determination of the alkaline reserve of the blood. CH. O. GUILLAUMIN. *Compt. rend. soc. biol.* **88**, 169-71(1923).—Reagents required: 0.02% phenol red (monosodium salt) soln., 0.9% NaCl adjusted to a  $p_H = 7.4$ ; exactly 0.01 N  $\text{H}_2\text{SO}_4$  and an approx. 0.01 N NaOH renewed frequently. This is daily retitrated, thus: to 5 cc. of the acid is added 0.5 cc. of indicator, then enough NaOH to give a  $p_H = 7.0$ . The titer is designated as  $5/n$ ,  $n = \text{cc. of NaOH}$ . The detn. is carried out as follows: To 1 test-tube (all tubes are of uniform size with a diam. of 16-18 mm.) are added 1 cc. indicator, 20 cc. of the NaCl soln. and 1 cc. plasma from blood obtained by venopuncture. Into another test-tube, graduated at 21 cc., are put 1 cc. plasma, 5 cc. 0.01 N acid and 1 drop of octyl alc. This is then evacuated, gently for the first min. and more vigorously for another 5 min. Then 1 cc. of indicator is added and NaOH and the tube filled up to

the 21-cc. mark. The  $p_H$  of this test-tube is now adjusted so that it matches exactly the color of the first. The alk. reserve in vols. of  $CO_2$  at  $0^\circ$  and 760 mm. Hg per 100 cc. plasma =  $22.4 (5 - mt)$ , where  $m$  = cc. NaOH and  $t$  = titer of alkali. Results thus obtained checked up well by the Van Slyke method.

S. MORCULIS

**Studies on hemoglobin. III.** An ultra-micro method for the determination of hemoglobin as a peroxidase. HSING WU. *J. Biochem. (Japan)* 2, 189-94 (1923); cf. *C. A.* 17, 1806.—**Principle.**—production of a brown color from solns. of benzidine dissolved in AcOH by the simultaneous action of hemoglobin and  $H_2O_2$ . **Solns. required.**—(1) 2 g. benzidine (high-grade) dissolved in 20 cc. glacial AcOH with the aid of heat; when cool this is dild. with 80 cc.  $H_2O$  and is shaken 10-15 min. with 0.5-1 g. of blood charcoal; filtered clear soln. is preserved in a brown bottle where it will keep for 2 weeks. (2) A 3%  $H_2O_2$  soln. the strength of which is detd. by titration with  $KMnO_4$ . (3) A 20% AcOH made by dissolving 1 vol. of glacial AcOH in 4 vols. of  $H_2O$ . (4) A standard hemoglobin soln. prepd. as follows: 100 cc. blood the hemoglobin content of which has been detd. by the oxygen-capacity method is measured into a 1. volumetric flask and dild. with 800 cc.  $H_2O$ ; to this is added 40 g. of NaF; when this is entirely dissolved (warming if necessary) the soln. is made up to vol. and filtered. The standard is prepd. from this stock by proper dildn. **Procedure.**—Dil. 1 cc. blood to 100 cc., then 1 cc. of the mixt. to 50 cc. thus giving a dildn. of 1:5000. Dil. the stock hemoglobin soln. so as to obtain a final concn. of 0.5%. Measure 2 cc. of benzidine soln. into 2 clean test-tubes graduated at 25 cc. Add to one 1 cc. of the standard and to the other 1 cc. of the dild. blood. Add now 1 cc.  $H_2O_2$  to each tube, mix well and after 15 min. make up to vol. with 20% AcOH, again mix well and compare colors in a colorimeter. Reading of the standard (20) divided by the reading of the unknown and multiplied by the % of hemoglobin of the blood from which the stock soln. was prepd. gives the % of hemoglobin in the unknown sample of blood. By this method the hemoglobin can be detd. in 0.0001 cc. blood. The colors produced by equiv. amts. of oxy-, met-, carbonyl-, and cyano-hemoglobin are the same, but a corresponding amt. of hematin gives only about 70% of the color. Acid when added to blood may split off hematin and thus diminish the color; benzidine seems to exert a protective action by combining with the hemoglobin and for this reason the blood should be added to the benzidine soln. Other things being equal the color developed is roughly proportional to the benzidine concn.; therefore, the benzidine should be measured as carefully as the blood soln.

S. MORCULIS

The determination of ammoniacal nitrogen in organic materials. E. SELLIER AND FROIDREVAUX. *Chimie et industrie* 9, 270-1 (1923); cf. *C. A.* 17, 409.—**Control.** A. P.-C.

Two new methods for fibrinogen estimation. Protein estimations in salt plasma. The utilization of serum for the quantitative determination of blood. G. LEENDERTZ AND B. GROMELSKI. *Arch. expl. Path. Pharm.* 94, 114-23 (1923).—Both methods involve the use of the refractometer, the fibrinogen content of the blood being detd. by the difference in the  $n_s$  between citrated plasma and citrated serum. G. H. SMITH

Viscometer (LECOMPTE DE NOÛY) 1.

ABDERHALDEN, EMIL: Physiologisches Praktikum. Chem., physikalisch-chem., physikal. u. physiolog. Methoden. 3rd revised edition. Berlin: Julius Springer. 349 pp.

GOURDAL: Dosage de l'urée dans le sang applicable a de très faibles quantités de sang. Paris: A. Maloine et fils. 92 pp.



## C—BACTERIOLOGY

A. K. BALLS

**New species of yeast of the genus *Debaryomyces* (*D. matrichoti*).** GRIGORAKI AND PEJU. *Compt. rend. soc. biol.* **85**, 459-62(1921); *Physiol. Abstracts* **7**, 142.—This yeast, isolated from human feces, inverts sucrose, weakly attacks mannose, but is without action on glucose, fructose, galactose, raffinose, and dextrin. H. G.

**Antiseptic power (antigenetic) of some aniline dyes.** J. BRIDRŮ. *Compt. rend. soc. biol.* **85**, 645-6(1921).—The dyes examd. were benzyl violet, hexamethyl violet, brilliant green, and methylene blue. H. G.

**Studies of bacterial toxins. III. Diphtheria toxin formation.** L. E. WALBUM. *Biochem. Z.* **134**, 601-5(1923); cf. *C. A.* **16**, 2881.—The toxicity of the filtered diphtheria toxin or ext. of macerated diphtheria bacilli is increased on mixing with usual peptone-bouillon or a soln. of Witte peptone. This substantiates the theory expressed in an earlier paper (*Z. Immunitäts.* **3**, 1909) that bacteria form and excrete non-toxic "Protoxin" from which (during growth) the toxin is formed outside the cell. F. S. HAMMETT

**A new biological reaction for cholera vibrio.** H. KODAMA AND H. TAKEDA. *Centr. Bakt. Parasitenk.* **1**, **88**, 513(1922); *Bull. mens. office intern. d'hyg. publ.* **14**, 1533(1922).—Cholera vibrio produces a diastatic enzyme of considerable power, which may be demonstrated by the following special medium: 1 g. Witte peptone, 0.5 g. potato starch, 2 cc. of 10%  $\text{Na}_2\text{CO}_3$ , 100 cc. of water. Sterilize in an Arnold sterilizer. Inoculate 5 cc. of the medium with material from an agar culture and exam. after 7, 24, 48, and 168 hrs. incubation for action on deposit of starch. Add 1 soln. and observe by the color when starch disappears. The cholera organism removes the starch in 24 hrs. The similar vibrios of Mechnikoff, Finkler-Prior and Dencke are readily distinguished by slower action. The anthrax, subtilis, coli, typhoid, paratyphoid, dysentery organisms, *Staphylococcus aureus* and wild yeasts have little or no action. JACK J. HINMAN, JR.

**Fat coloration in yeast as a criterion of age, quality, and degeneration.** BERNFELD. *Woch. Brau* **39**, 195(1922).—The presence of fat in yeast cells may be rendered evident by staining with either alkanina or soudan III. An aq. suspension of the yeast similar in consistency to that leaving the separators is stirred with alc. soln. of soudan III, satd. in the cold, this being added drop by drop until an orange-red coloration is obtained; the action of the coloring matter is continued for 30-40 minutes. The extent to which the color is taken up increases with the no. of generations; thus, if the time during which the dye acts is const., cells of the first generation may show no color, while those of the third generation exhibit small, slightly tinted points and those of the fourth larger and distinctly colored fat drops. Small cells are usually richer in fat than older ones. The results obtained may be vitiated if the staining is prolonged, owing to the toxic action of the alc. or dye coming into play. If 0.005% of methylene blue is mixed with the soudan III, dead cells may be detected at the same time. J. S. C. I.

***Saccharomyces odessa*, nov. sp.** H. SCHNEGG AND F. OEHLEKERS. *Z. ges. Brauw.* **45**, 92-6, 106-7, 111-13(1922).—This yeast, isolated from the beer of an Odessa brewery, consists normally of almost round or slightly oviform cells and on 8-10% beer wort forms a slight film and a ring growth which gradually extends to the rim of the culture vessel. Both the film and the ring contain many long, sausage-shaped cells and occasional giant cells. The organism readily forms from 1 to 3 spores per cell, these being obtained better on filter paper than on plaster blocks and in greater abundance if the yeast is previously grown in a strong rather than in a weak wort. The giant colonies formed on wort-gelatin closely resemble those obtained with Froberg yeast. The degree of fermentation obtained with 7.9% wort is about 62%, and the yeast ferments sucrose, dextrose, levulose, maltose and mannose readily, galactose and raffinose slightly, and lactose, mannitol, dextrin, glycerol, amygdalin and inulin not at all.

The organism is distinctly thermophilic and reproduces most rapidly at 32°. The spores exhibit extremely high refractivity, and under suitable conditions some of the mother cells contg. spores are capable of germination without the spores themselves undergoing alteration.

J. S. C. I.

**Notes on d'Herelle's phenomenon.** Adaptation of bacteriophage antagonistic to *Bacillus dysenteriae* and other bacilli to various cocci. Development of a polyvalent bacteriolysant. E. B. MCKINLEY. *J. Lab. Clin. Med.* 8, 311-7(1923).—Bacteriolysant originally antagonistic to the bacillus of dysentery (Shiga) by adaptation became antagonistic to the meningococcus and other cocci. It is suggested that there is only one bacteriophage and this can acquire activity against any microorganism. E. R. LONG

**The relation of hydrogen-ion concentration to the growth curve of microorganisms of the dysentery-colon group.** K. G. DERNBY AND CARL NÄSLUND. *Z. Immunitäts.* 35, 450-4(1923).—The optimum reaction for the growth of bacteria of the dysentery-colon group is close to neutrality. The medium should have an initial H-ion concn. of pH 7.0-7.5, in the case of non-sugar culture fluids, and 7.5-8.0 in sugar-contg. media, as acid is produced from sugar.

E. R. LONG

**Formation of anthranilic acid from l-tryptophan through the action of Subtilis bacteria.** TAKAOKI SASAKI. *J. Biochem. (Japan)* 2, 251-4(1923).—In expts. with *B. proteus* S. found the conversion of l-tryptophan into l-indolelactic acid. Similar expts. were instituted with tyrosine and phenylalanine using *B. subtilis*. But when S. attempted to isolate the l-indolelactic acid by his usual procedure of pptn. with basic Cu acetate an admixt. was discovered which did not behave like the l-indolelactic acid. Only a few exs. were at first isolated which permitted its identification as anthranilic acid. By substituting CuSO<sub>4</sub> as the pptg. agent a much larger yield of this substance was obtained which made a more careful examn. possible. The substance m. 144-5° and its elementary analysis coincided definitely with that of anthranilic acid.

S. MORGULIS

**The production of uracil from cytosine through putrefaction.** RYŪZO IWATSURU AND MASAJI CHIKANO. *J. Biochem. (Japan)* 2, 279-81(1923).—2.2 g. of cytosine was dissolved in 200 cc. of a nutritive medium and the whole was then infected with a drop of putrefied pancreatic mixt. After 34 days of incubation at 37° there was still present 0.15 g. cytosine while the remaining 0.7 g. was in the form of uracil. This transformation occurred in 2 expts.

S. MORGULIS

**Variations in hydrogen sulfide productions by bacteria.** F. W. TILLEY. *J. Bact.* 8, 115-20(1923).—When used in Pb(OAc)<sub>2</sub> agar, different peptones now available in this country yielded extremely variable results so far as H<sub>2</sub>S production is concerned. In some cases different samples of the same peptone failed to give concordant results.

JOHN T. MYERS

**Physiological youth in bacteria.** J. M. SHERMAN AND WM. R. ALBUS. *J. Bact.* 8, 127-39(1923).—There is a difference in the physico-chem. condition of bacterial cells of different ages. The young cells are more sensitive to phenol, are more readily agglutinated by acid, and are more easily killed by cold, heat, distd. water, and 2% NaCl.

JOHN T. MYERS

**Studies on salt action. VI. Stimulating and inhibiting effect of certain cations on bacterial growth.** MARGARET HOTCHKISS. *J. Bact.* 8, 141-62(1923); cf. Winslow and Falk, *C. A.* 13, 2694.—Salts dissolved in a 1% peptone soln. medium exerted an influence on the growth of *B. coli* depending on the sp. salt and its concn. Each salt was so toxic at some concn. as completely to inhibit growth. The salts of the alk. metals and the alk. earths were much less toxic than salts of the heavy metals. The salts of the first group yield neutral solns. and those of the second group give acid solns. owing to hydrolysis. The toxicity is probably largely due to the H-ion concn. The

anion in every case was Cl. In 15 of the 23 chlorides studied a concn. was found which stimulated growth. The stimulating salts included not only Na, K, NH<sub>4</sub>, Li, Sr, Mg, Ca, and Mg, but such toxic salts as those of Ti, Sn, Ni, Pb, Co, and Hg. The stimulating concns. for the latter group were very low, 0.00005 *M* in the case of Ce and 0.00001 *M* for Hg, while for K and Na 0.25 *M* was stimulating. JOHN T. MYERS

The relation between chemical constitution and antiseptic action in the coal tar dyes. THOMAS H. FAIRBROTHER AND ARNOLD RENSHAW. *J. Roy. Soc. Arts* 71, 281-95, 302-20(1923).—Chiefly a repetition, cf. *C. A.* 16, 2709, 3994. Results with some additional dye derivs. are tabulated.

GEORGE ERIC SIMPSON

Mechanism of bacteriostasis. J. W. CHURCHMAN. *J. Exptl. Med.* 37, 543-51 (1923).—Between Gram-positive and -negative organisms, gentian violet exhibits the same type of selective activity whether the dye be added to the media on which the bacteria are planted unstained (extrinsic bacteriostasis) or the organisms be stained with it before being planted on plain agar (intrinsic bacteriostasis). In both instances the Gram positives are inhibited and the Gram negatives unaffected. Between Gram-positive spore-bearing aerobes and the commoner Gram-negative bacteria, acid fuchsin, related sulfonic substances and the flavines exhibit one type of selective activity when the dye is added to the media and the opposite type when it is added directly to the bacteria. In the former case the Gram-positive spore bearers are inhibited and the Gram negatives unaffected, while in the latter case the reverse is true. Selective bacteriostasis is not necessarily conditioned by selective penetrability. Stained organisms may grow, and dyes which do not stain well may inhibit reproduction. There is evidence that the phenomena of bacteriostasis may be due to changes effected by the dye at the surface of the organisms.

C. J. WESS

HEIM, LUDWIG: *Lehrbuch der Bakteriologie mit besonderer Berücksichtigung der Untersuchungsmethoden, Diagnostik und Immunitätslehre.* Stuttgart: F. Enke. 726 pp.

MOORE, C. G. and PARTRIDGE, WM.: *Bacteriology and Parasitology.* New York: W. Wood & Co. 30 pp. \$1.75.

#### D—BOTANY

B. M. DUGGAR

Differences effected in the protein content of grain by applications of nitrogen made at different growing periods of the plant. W. F. GERICKE. *Soil Science* 14, 103-9(1922).—Spring wheat, oats, winter wheat, and rye were grown in 1-gal. stone jars filled with a soil low in nitrogen. One set of 3 jars of each cereal received NaNO<sub>3</sub> at the rate of 100 lbs. per acre at the time of planting; a second set was similarly treated 2 weeks after planting, and other sets at later periods. The size of grain was not markedly affected. The yield was greatly influenced (data to be reported later). The protein content of the grain showed increases of from 8.9% to 15.2% in spring wheat, from 13.4% to 17.9% in winter wheat, 7.5% to 17.2% in oats and 9.5% to 14% in rye. The higher content was always found in the sets receiving the later applications, which were made from 108 to 121 days before harvest. Such differences in the natural environment may be responsible for differences commonly considered genetic. R. B.

The effect of lime, leaching, form of phosphate and nitrogen salts on plant and soil acidity and the relation of these to the feeding power of the plant. F. C. BAUER AND A. R. C. HAAS. *Soil Science* 13, 461-80(1922).—Soy beans and corn were grown in sand cultures variously treated with rock phosphate, acid phosphate limestone, NaNO<sub>3</sub>, and NH<sub>4</sub>NO<sub>3</sub>. The acidity of the medium and of the plant juices were both affected by these treatments. This change in acidity was closely related to the feeding power of the plant. The removal of the Ca ion either by leaching or by absorption by the

plant increases the soly. of rock phosphate. When  $\text{NH}_4\text{NO}_3$  was used in connection with rock phosphate greater acidity was developed and in some cases the combination was more efficient than acid phosphate.  $\text{NH}_4\text{NO}_3$  + acid phosphate produced an acidity great enough to retard growth. Marked differences in the  $p_H$  of the soil caused only a slight change in the  $p_H$  of the plant juices. The titratable acidity showed wider variations.

R. BRADFIELD

Ash image and its diagnostic bearing. GUSTAV KLEIN. *Pharm. Presse* 27, No. 17, 3-4(1923).—It is shown in several examples how the ash of plant tissues, ordinarily serving only in the qual. and quant. detection of inorg. constituents, is sufficiently characteristic to permit recognition of certain species, genera and families. W. O. E.

Composition of the crystalline spherites sometimes occurring in the root of *Althaea officinalis* and *A. rosea*. I. R. FAHEY. *Pharm. Presse* 27, No. 23, 2(1922).—The observed crystals are believed to be Ca phosphate or malophosphate. W. O. E.

Influence of the salinity of sea water on the assimilation of chlorophyll by algae. R. LÉONARD. *Compt. rend. soc. biol.* 85, 222-4(1921); *Physiol. Abstracts* 7, 148.—C assimilation of *Ulva lactuca* and *Fucus serratus* increases with decreasing density of the sea water up to a max. when the density is 1.010. In more dil. soln. the assimilation decreases. The content of carbonate and bicarbonate may be a factor influencing the result.

H. G.

Carbon dioxide assimilation in sun and shade leaves. M. G. STRÄLVELT. *Medd. Statens Skärgörsökningsanstalt, Stockholm* 1921, 221-80; *Physiol. Abstracts* 7, 148.—The following values are given of mg. of  $\text{CO}_2$  assimilated per hr. per g. fresh weight:

	Light intensity % of open daylight										
	0.	10.	20.	30.	40.	50.	60.	70.	80.	90.	
<i>Picea excelsa</i> :											
Sun leaves.....	-0.20	-0.07	0.34	0.58	0.78	0.95	1.10	1.23	1.33	1.42	
Shade leaves.....	-0.27	+0.47	0.93	1.24	1.47	1.64	1.78	1.89	1.97	2.00	
<i>Pinus silvestris</i> :											
Sun leaves.....	-0.37	+0.40	0.89	1.24	1.54	1.80	2.02				
Shade leaves.....	-0.20	+0.72	1.25	1.62	1.91	2.15	2.35	2.53	2.69	2.81	

It is remarkable that the maximal  $\text{CO}_2$  assimilation is first attained in full daylight.

H. G.

Permeability of plant protoplasts to sulfonic acid dyes. R. COLLANDER. *Jahrb. wiss. Bot.* 60, 354-410(1921); *Physiol. Abstracts* 7, 143.—Colorimetric estns. of the quantity of dye absorbed by a variety of plant cells showed that in general the sulfonic acid dyes are absorbed very slowly and only to a slight extent. A few exceptions are recorded. The results are discussed in their relation to various theories of permeability.

H. G.

Localization of the enzymes and diastatic processes in the Calabar bean. MORVILLEZ and POLONOVSKI. *Compt. rend. soc. biol.* 85, 183-4(1921); *Physiol. Abstracts* 7, 141.—Genserine as well as eserine is found in Calabar bean. It is probably an oxide of eserine. The testa will turn guaiacum blue in absence of  $\text{H}_2\text{O}_2$ . This property is lost after heating to 100°. The localization of oxidases in the seed was studied by means of benzidine acetate. Genserine is found chiefly in the inner side of the testa, also in the cotyledons.

H. G.

Dehydration of certain plant tissues. V. R. BOSWELL. *Bot. Gaz.* 75, 86-94 (1923).—Cabbage and tomato leaves of known degrees of hardness were used. A few leaves were taken from the plants for each sample, placed in shallow weighing bottles with covers, and weighed. The leaves were next spread in an oven (kept at 60°) on a shelf covered with wire gauze. The samples were dried 15 min., removed, put in bottles, covered, cooled and weighed. The drying was repeated until a const.

wt. was reached. In every case the hardy tissue lost water less rapidly than the tender tissue. In very hardy tissues the loss of water is so slight as to suggest some colloidal combination.

BENJAMIN HARROW

**Fixation of nitrogen by plants.** EDWARD WHITLEY. *Nature* 111, 187(1923).—In connection with Lipman and Taylor's announcement that the wheat plant has the power of fixing N, W. points out that B. Moore "obtained similar results on other plants" (see *C. A.* 14, 2359; 15, 1335, and Moore's book on Biochemistry, *C. A.* 16, 1259). Moore concluded that "both the lower and higher plants do build up nitrites and nitrates and form org. nitrogenous compds. from the free N of the atm." B. H.

**Cellular elements in the cytoplasm of plants.** Chondriomes, vacuoles, and lipid granules. A. GUILLIERMOND. *Arch. biol.* 31, 1-82(1921); *Physiol. Abstracts* 7, 64-5 (1922).—A discussion of the structures in the cytoplasm with special reference to the origin of vacuoles, and of fat and glycogen in fungi, the formation of anthocyan, chondriomes, and metachromatin.

JOSEPH S. HEPBURN

**Biochemical observations on certain insectivorous plants.** J. S. HEPBURN. *J. Franklin Inst.* 194, 771-81(1922).—The liquor from pitchers of *Nepenthes*, which were entirely free from insect captures, contained a protease which exerted its activity in a slightly acid medium. Catalase, urease, esterase, diastase, invertase, maltase, lactase, emulsin, phosphates, and saponins were not present in the pitcher liquor; chlorides were present. A substance, which reduced Benedict alk. Cu soln., was frequently, but not invariably, present in the pitcher liquor; it was probably sugar derived from the nectar. A composite sample of the secretion of the leaves of the Venus fly trap (*Dionaea muscipula*) contained a protease active in the presence of 0.2% HCl. The leaves of this plant, gathered in its native habitat in May and air-dried, had the following percentage compn.: H<sub>2</sub>O 8.38, total solids 91.62, crude protein 8.31, crude fat 11.18, crude fiber 11.58, N-free extractives 55.53, total ash 5.02, insol. ash 3.32, sol. ash 1.70. The sol. ash present in 1 g. of air-dried leaves required 1.45 cc. of 0.1 N HCl for its neutralization to methyl orange, while the insol. ash required 6.14 cc. A bibliography is appended.

JOSEPH S. HEPBURN

**Influence of increased temperature on the cells of the root meristem of *Allium cepa*, a contribution to the analysis of the processes of nuclear division.** F. WASSERMANN. *Anat. Anz.* 54, 163-75(1921); *Physiol. Abstracts* 7, 64(1922).—High temps. give rise to changes in the metabolism of the cytoplasm; as a result of these changes, cell division is completely inhibited.

JOSEPH S. HEPBURN

**Some characteristics of the virus diseases of plants.** H. J. BUTLER. *Science Progress* 17, 416-31(1923).—Review. Some attention is paid to the chem. changes in the tissues of the diseased plants.

JOSEPH S. HEPBURN

**Fluorine in Spanish grapes.** MARTINIANO LEGUIGAMÓN PONDAL. *Anal. asoc. quim. Argentina* 10, 57-73(1922).—F is found to be a normal constituent in Spanish grapes. A method is described for its detection, using the etching action of HF.

J. C. S.

**Influence of temperature on the diminution of the nucleus through inanition in the bean.** A. MAIGE. *Compt. rend. soc. biol.* 88, 97-9(1923).—Inanition of the growing bean was produced through the removal of the cotyledons. The diminution of the nuclear and nucleolar mass was accelerated by an increase in temp. just as the catabolic processes were increased. The presence of sugar diminishes the rate of loss of mass of the nucleus.

S. MORGULIS

**Chemical studies of corn pollen. 1. Isolation of phytosterol and inositol.** SU-CURU MIYAKE. *J. Biochem. (Japan)* 2, 27-32(1922).—The sample used for the analysis was from a variety of dent corn planted at Sapporo, Japan, in August 1921 and 1922. The pollen contained water 43.42, crude protein 14.33, crude fat 1.55, crude fiber 5.12,

crude ash 4.79, N-free ext. 33.79%. Pure protein formed 10.32, starch 16.19, dextrin 0.80, reducing sugar (as glucose) 0.59, non-reducing sugar 7.80, pentosan 5.73%. Phytosterol was isolated as follows: The pollen sample was steeped in ether, the ether filtered off and dried. The fat residue was saponified by boiling with alc. KOH on a water bath, and the alc. was completely evaporated. After dissolving the residue in water the unsaponifiable portion was again extd. with ether. The crystals obtained by evap. this ether ext. were dissolved in abs. alc., purified with charcoal, and white crystals, m. 137.5, remained after the alc. was evapd. The acetate, prepd. by boiling with  $\text{Ac}_2\text{O}$ , m. 131°. When wetted with a few drops of  $\text{H}_2\text{SO}_4$  the phytosterol became rose-red, turning to blue on the addition of an  $\text{I}_2$  soln.; it dissolved in 2 cc.  $\text{CHCl}_3$  and shaken with an equal vol. of  $\text{H}_2\text{SO}_4$  a brown color rapidly developed in the  $\text{CHCl}_3$  while the  $\text{H}_2\text{SO}_4$  presented fluorescence; also the Liebermann reaction with  $\text{Ac}_2\text{O}$ , which produces a violet-pink color, was obtained. Inositol was likewise isolated. The pollen residue which was left over after the ether extn. was heated on a boiling water bath under a reflux condenser for 3 hrs. with 3 l. 90% alc. This was filtered through a Buchner funnel and the operation repeated 3 times with fresh alc. The alc. exts. were concd. to a sirup by vacuum distn.; this was purified by 80% and later by 95% alc. The residue was well mixed with the alc. and allowed to stand overnight. It was filtered from the pptd. matter and distd. under vacuum. From the purified sirup in 2 weeks time small crystals were obtained. These were dissolved in a small amt. of  $\text{H}_2\text{O}$ , purified with charcoal, and recrystallized from the soln. by abs. alc. White crystals, m. 225°, were obtained. It did not reduce Fehling soln. but produced a silver mirror when heated with ammoniacal silver soln.; it gave the Scherer reaction (ros-red color resulting when the crystals evapd. with a few cc.  $\text{HNO}_3$  are treated with ammoniacal  $\text{BaCl}_2$ ) and the Seidel reaction (red color obtained when a few mg. are heated over open flame, then treated with 3-4 cc. glacial  $\text{CH}_3\text{COOH}$ , 0.5 cc.  $\text{H}_2\text{O}$  and a drop of 10% Sr acetate); did not rotate polarized light; mol. wt. by freezing point method was 178.

S. MORGULIS

The behavior of chlorides in the cell sap of *Nitella*. M. IRWIN. *J. Gen. Physiol.* 5, 427-8(1923).—Cl was detd. by counting the no. of drops of 0.002 0.0006  $M$   $\text{AgNO}_3$  soln. required to titrate the cell sap contg.  $\text{K}_2\text{CrO}_4$  as indicator. The av. Cl content of the sap was 0.128  $M$ , a much higher concn. than the water in which the plant lives. Cl accumulates in the plant during growth. Attempts to increase the Cl content by placing the plant cells in solns. contg. Cl were unsuccessful. The exosmosis of Cl from injured cells can be followed quant. Upon cutting off one end of the cell, a wave of injury passes toward the uninjured end accompanied by a progressive exosmosis of Cl. These and other expts. suggest that the entrance and accumulation of cations (except  $\text{H}^+$ ) is favored by solns. of high  $p_{\text{H}}$ , that of anions (except  $\text{OH}^-$ ) by solns. of low  $p_{\text{H}}$ . Other possibilities are: That the entrance of cations may also involve the simultaneous penetration of  $\text{OH}^-$ ; the entrance of anions may be accompanied by the penetration of  $\text{H}^+$ ; the penetration of an ion may involve the exosmosis of another similarly charged ion.

CHAS. H. RICHARDSON

Starch of the Floridean algae. G. MANGENOT. *Compt. rend.* 176, 183-5(1923); cf. *C. A.* 16, 4246.—This study is mainly histological. Chemically these starches are hydrolyzed to hexoses and behave as typical starches. The iodine reaction distinguishes them slightly. Their essential characteristics are cytologic in that their mode of formation is different from that of common starch which arises in the chloroplasts. The Floridean starches arise from the cytoplasm with a probable participation of the nucleus.

L. W. RIGGS

Influence of hexamethylenetetramine and of formaldehyde upon the internal morphology and upon the chemism of the bean. E. NICOLAS AND G. NICOLAS. *Compt.*

rend. 176, 404-7(1923); cf. C. A. 17, 796.—These substances have been shown to be foods for the hean plant. They not only cause an increase in wt. and a large development of leaf surface, but they are utilized for the differentiation and even lignification of the wood and of the pericycle, also in the formation of starch. L. W. RIGGS

Evolution of starch grain in the potato tuber. L. LINDET AND P. NOTTIN. *Compt. rend.* 176, 149-55(1923); cf. Dangeard, C. A. 14, 1699.—A histological study.

L. W. RIGGS

Urease of fungi. A. GORIS AND P. COSTY. *Compt. rend.* 176, 412-4(1923); cf. C. A. 17, 792.—This study was made chiefly on *Boletus edulis* hult. The urease of fungi is not entirely destroyed by a temp. of 76°. The optimum temp. of action measured by ability to hydrolyze urea is 38°. Mineral or org. acids act energetically upon urease; a concn. of 2 cc. 0.1 N HCl in 100 cc. arrests, and 3 cc. entirely prevents its action. The action of acids at 37° is much more rapid than that at ordinary temp. To produce the same results as 1 cc. of 0.1 N HCl or H<sub>2</sub>SO<sub>4</sub> would require 2, 2.6, 3.2 and 12 cc., resp., of 0.1 N tartaric, lactic, citric and acetic acids. Salts of alkalies have much less action on urease than acids of equiv. concn., while urease can withstand a concn. of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 10 times as great as that of Na<sub>2</sub>CO<sub>3</sub> without losing its activity. Of salts of the 3 common mineral acids, those of Ca have a strong retarding action upon urease; then follow in decreasing order those of Na, K, NH<sub>4</sub> and Mg. Antiseptics act on urease much as on other enzymes.

L. W. RIGGS

The structure of the starch grain. O. L. SPONSLER. *Am. J. Botany* 9, 471-92 (1922).—A brief history is given. The X-ray method was used to det. the crystal structure of the grain. The method consisted in photographing the X-rays which are reflected from the various at. planes of a crystal. Two points seem to have been fairly definitely proved: (1) that there is, within limits, a regular and fairly uniform arrangement of atoms in the starch grain; and (2) that this regularity is destroyed by crushing the grain, which leads to the additional statement that regularity is not that of cryst. structure. These statements oppose the spherocrystal theory of Schimper and Meyer while they favor the assumption made by Kahsch in 1863 that the grains have a phys. uniformity which, however, is not sufficiently regular to assign crystallographic axes to them. Or, it may be that, instead of planes, such as are found in crystals, the regularity takes the form of curved layers.

F. M. SCHERTZ

Fluorescing substance in mandarin orange peel. MASAMICHI KIMURA AND GISA-BURO NAKAMURA. *Japan J. Physics* 1, 4t-8(1922).—A fluorescing substance, sol. in C<sub>6</sub>H<sub>6</sub>, slightly sol. in Et<sub>2</sub>O and almost insol. in EtOH, has been found in the peel of the mandarin orange, *Citrus sinense*, bitter orange, etc. The color of the fluorescence, excited by the light of an Fe arc filtered through a black glass contg. a NiO as 1 of its coloring substances, was bright yellowish green; its intensity was very great. This bright fluorescence died out gradually, in 1 prepn. being reduced to 0.5 its initial intensity after 15 min. The rays capable of exciting the fluorescence of this substance should have a wave length shorter than  $\lambda$  4050. The decay of fluorescence is accompanied by change in color. The absorption spectra were also examd. C. J. WEST

Comparative plant chemistry. IV. *Juncus effusus* L. JULIUS ZELLNER. *Monatsh.* 43, 120-3(1922); cf. C. A. 16, 1969.—Chem. examn. of the green stems of *Juncus effusus* L. gathered in Sept. gave: petrol. ether ext., 2.18%; Et<sub>2</sub>O ext., 1.72; EtOH sol., 16.78, of which 1.07 was phlobaphene, 3.04 dextrose; total H<sub>2</sub>O sol., 21.21; membrane material, 63.96, of which 35.06 was crude fiber, 20.09 pentosans, 1.50 methylpentosans; total nitrogen, 1.47; total ash, 4.69.

C. J. WEST

Plant incrustations. III. E. SCHMIDT, E. GREISLER, P. ARNDT AND F. IHLOW. *Ber.* 56B, 23-31(1922); cf. C. A. 16, 273, 949.—Wood is extd. first with an 8% soln. of ClO<sub>2</sub>, and then with hot, 2% Na<sub>2</sub>SO<sub>3</sub>. The exts. are purified by various processes,

including ordinary dialysis, electroösmosis (C. A. 16, 863, 1531), evapn. to dryness and extn. with alc. The last named process seps. the polysaccharides from the unknown substances produced by the decomposing action of the  $\text{ClO}_2$ . The constituents of neither fraction are reported in the present paper. As an example, 300 g. beech wood yielded 105 g. lignin, consisting of 72 g. polysaccharides and 23 g. alc.-sol. products. The method is applicable to the study of plants from the higher fungi up. J. J. W.

Notes on the active principles of some South African plants. I. Wild celery (*Peucedanum galbanum* (L.) Benth. and Hook). C. F. JURITZ. *Chem. News* 126, 67-9 (1923).—The volatile oil was prepd.;  $d_{24} = 0.847$ ;  $n_D^{20} = 1.4742$ ; b.  $85^\circ$ , and fractionates. It has no vesicant properties; hence the blistering action of the leaves cannot be due to the oil. The ext. of the plant is diuretic. II. Slangkop (*Urginea macrocentra*, Baker). *Ibid* 69-70.—Many species of this genus in South Africa are very poisonous to stock. *U. macrocentra* (J. W. C. Dunn, *Trans. Roy. Soc.* 9, 197 (1921)) contains a glucoside very similar to digitalis in its properties, and can be substituted for squill (*U. scilla*) in pharmacology. III. Mafeura bean (*Trichilia emetica* Vahl). *Ibid* 86-7.—This bean is the seed of the Cape mahogany. The cortex is poisonous, but the oil is not, and is used in cooking and in soap making. J. J. WILLAMAN

Lesser contributions to plant chemistry. E. O. VON LIPPENMANN. *Ber.* 55B, 3038-41 (1922).—(1) Sucrose was identified as the main constituent of nectar oozing from the inflorescences of a thimble plant. (2) Trehalose was isolated from grains of ergot found in a species of wild oats. (3) A white, transparent gum, exuding from a quince tree killed by gas, gave on hydrolysis only *i*-galactose. (4) The principal acid of the service berry is malic. Other acids present are citric, tartaric, and succinic. J. J. W.

Plant indicators of soil types (KELLEY) 15. *d*-Quercitol in the seeds of *Achras sapota* (HAAR) 10.

FURST, ARNOLD: *Éléments de chimie horticole*. Nauur: Impr. H. Dubois. 144 pp.

MOLLIARD, MARIN: *Nutrition de la plante*. III. Utilisation des substances ternaires. Paris: Octave Doin. 320 pp. Fr. 14.

## E—NUTRITION

PHILIP H. HAWK

### NORMAL

Metabolism in China. B. E. READ AND S. Y. WANG. *Philippine J. Sci.* 22, 127-37 (1923).—The urinary findings check other investigations on Asiatics. They are probably due to a high cereal diet, since unlike other investigations on Asiatics, they were obtained during the dry cold season. II. V. ATKINSON

Vitamins. E. ROTHLIN. *Schweiz. med. Wochschr.* 52, 195-201, 219-25 (1922); *Physiol. Abstracts* 7, 184.—Summary. H. G.

How are our principal foodstuffs oxidized and converted into one another in the animal organism? F. KNOOP. *Klin. Wochschr.* 2, 60-3 (1923).—A review. M. H.

The variations in the acidity of the urine after the ingestion of an unbalanced diet. M. HASSELMANN. *Klin. Wochschr.* 2, 122-3 (1923).—A urine with a titration acidity of 228 and  $p_H$  7.0 was excreted by a normal man, after the ingestion of a diet consisting largely of potatoes (1500 g. per day). After the ingestion of a diet consisting largely of oats, the urine had a titration acidity of 350 and  $p_H$  5.5. A diet consisting largely of meat gave the lowest titration acidity—200—with a  $p_H$  of 6 to 7. MILTON HANKE

The digestibility of fats. C. F. LANGWORTHY. *Ind. Eng. Chem.* 15, 276-8 (1923).—The digestibility of 23 animal, 34 vegetable, and 6 hydrogenated fats was studied by feeding amts. ranging from 50 to 115 g. or more to students or lab. assistants. The



fats, disguised in cornstarch pudding, were fed together with a simple standard basal ration. Feces were analyzed by standard methods. Results showed no very great differences in the digestibility of fats studied. To some extent the thoroughness of digestion was inversely proportional to the m. p. of the hydrogenated fats; those hydrogenated to a definite m. p. and those made by mixing soft and hard fats showed no essential differences in thoroughness of digestion. No laxative effect was observed except in the case of a few fats, e. g., cacao butter and goose fat. The results justify the important place fats occupy in the usual dietary. C. J. V. PETTIBONE

**The pathological anatomy of ophthalmia produced by diets containing fat-soluble A, but unfavorable contents of certain inorganic elements.** SHINNOSUKE MORI. *Am. J. Hyg.* 3, 99-102(1923).—The pathol. changes in the eyes of rats developing ophthalmia as a result of diets contg. adequate fat-sol. A, but unfavorable salt mixts. are detailed. Clinically and pathologically the condition is the same as that resulting from insufficient fat-sol. A. GEORGE ERIC SIMPSON

**Organic foodstuffs with specific action. XIX. Feeding experiments with the tissues of pigeons fed upon polished rice and with tissues of those on a normal diet.** EMIL ANDERHALDEN. *Arch. ges. Physiol.* (Pflüger's) 197, 89-96(1922); cf. C. A. 17, 805.—Pigeons were fed upon polished rice and later one group was fed the tissues of normally fed pigeons, the other, tissues of pigeons which had been upon a rice diet. Both groups reacted in essentially the same manner. **XX. Comparative feeding experiments with various pure foodstuffs.** *Ibid* 97-104.—The manifestations of alimentary dystrophy seen with polished rice diets also appear when pure foodstuffs (casein, sugars, fatty acids, mineral salts) constitute the sole food supply. **XXI. Experiments with pure foodstuffs with an excess of carbohydrate or fatty acid-glycerol mixture.** *Ibid* 105-20.—Alimentary dystrophy results, not only from the lack of sp., although unknown, substances but also from an excess of carbohydrate. **XXII. Feeding of pigeons with meat, with and without the addition of supplementary substances.** *Ibid* 121-30.—Pigeons may be maintained upon completely digested proteins (meat) or upon meat and glucose. The addition of carbohydrates or fatty acid-glycerol mixtures proved particularly satisfactory. G. H. SMITH

**Calcium metabolism.** ADOLF SINDLER. *Arch. ges. Physiol.* (Pflüger's) 197, 386-403(1922).—The Ca balance is to a high degree dependent upon the meat intake; an increase in the proportion of the Ca, when added to a diet rich in meat, is less efficient in improving the balance than is a decrease in the amt. of meat consumed. Exptl. introduction of Ca causes a Ca retention, but in adults the excess of the introduced salt is uniformly eliminated, by the kidneys or intestine, within a few days after the suspension of the Ca ingestion. The exptl. introduction of Ca may cause an improvement in the  $P_2O_5$  balance, and the Ca retention is accompanied by a simultaneous retention of K. When a mol. concn. is maintained in the blood there is a compensatory elimination of NaCl. G. H. SMITH

GOUDISS, CHARLES H.: **Eating Vitamines. How to Know and Prepare the Foods that Supply these Invisible Life Guards, with 200 Tested Recipes and Menus for Use in the Home.** New York: Funk & Wagnalls. 98 pp. \$1.25.

HOLT, L. E.: **Food, Health and Growth: A Discussion of the Nutrition of Children.** New York: Macmillan Co. 273 pp. Reviewed in *Expt. Sta. Record* 47, 766 (1922).

McCARRISON, R.: **Studies in Deficiency Disease.** London: Henry Frowde and Hodder & Stoughton. 270 pp. Reviewed in *Expt. Sta. Record* 47, 369(1922).

MOLS, JOSEPH PETER: **Proper Nutrition.** Buffalo, N. Y.: The Author.

## F—PHYSIOLOGY

ANDREW HUNTER

**Secretions of the stomach in man with special regard to psychic influences.** II. G. R. HEYER. *Arch. Verdauungs-krankh.* 29, 11-27(1921); *Physiol. Abstracts* 7, 182; cf. C. A. 15, 2479.—The stomach produces juice of different HCl content, depending on the food suggested. Those differences are seen at the beginning of the secretion, when there cannot be fatigue. Suggestions of pain cause an immediate stoppage of secretion. The suggestion of joy causes also inhibition, but of slower onset. All psychic excitations act disadvantageously on the stomach. Injections of atropine before the suggestion partly inhibit the appetite juice. An injection immediately after the suggestion acts similarly, but if the flow is well in progress atropine has no effect. Pilocarpine stimulates secretion somewhat, but has no influence on "suggestion juice." H. G.

**Active and combined adrenaline.** II. E. NICOLAS. *Compt. rend. soc. biol.* 86, 849-50(1922); *Physiol. Abstracts* 7, 257-8.—The expts. of Abelous and Soula (C. A. 16, 2174) were vitiated by the fact that the serum used by them contained a small amt. of  $\text{CH}_2\text{O}$ . H. G.

**Changes in the reaction of urine during twenty-four hours.** N. K. KOLZOV AND S. N. SKADOVSKI. *Bull. Inst. Exptl. Biol. (Moscow)* 1, 31-5(1921); *Physiol. Abstracts* 7, 192.—The acidity is lessened by food and by the night's rest; it rises with activity and hunger. Frequent meals are recommended in nephritis. H. G.

**Electric charges of the red blood corpuscles.** K. KOSAKA AND M. SEKI. *Comm. of the Okayama Med. Soc.* No. 372(1921); *Physiol. Abstracts* 6, 193.—By observations on corpuscle suspensions under the microscope, and also on their behavior in the usual electrophoresis U-tube, it was found that when suspended in 0.9% NaCl or 1.15% KCl solns. the erythrocytes of all the animals tended to move towards the anode, with the exception of those of the rabbit. The rate of movement of the corpuscles of the various animals seemed not to depend to any extent upon their resp. diams. In HCl,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{K}_2\text{SO}_4$  the movements observed were similar to those in the NaCl soln. In solns. of  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ , and  $\text{SrCl}_2$  the movement was also in the same direction, but slower, the corpuscles of the rabbit remaining practically stationary in these solns. In  $\text{COCl}_2$ ,  $\text{NiSO}_4$ ,  $\text{MnSO}_4$ , and  $\text{MnCl}_2$  solns. all the corpuscles tried moved towards the anode, including those of the rabbit. Acids seem to favor movement towards the cathode; alkalis favor the movement in the opposite direction. In 9.5% soln. of cane sugar or isotonic solns. of other sugars, corpuscles of all species wander to the anode, but addn. of salts to the sugar soln. tends to reverse the direction of movement. Addn. of corpuscles to an acid soln. generally tends to lower the acidity, and similarly they tend to diminish the alk. of an alk. soln. Rabbit corpuscles are exceptional in influencing the acidity of an acid soln., but possess little power of neutralizing alkalis; the reverse behavior is shown by dog corpuscles. The taking up of Cl ions by the corpuscles was also studied, and explained in terms of an actual passage of the ions through a limiting membrane into the mass of the corpuscle. The phenomena in general are explained in terms of a theory of selective ionic permeability of the corpuscle membranes. With regard to hemolysis, it seems that on the whole those corpuscles which are most strongly negatively charged are most easily dissolved by acids, the least powerfully charged dissolved most readily in alkalis. Ions of metals with a lower soln. pressure than that of H are more powerful hemolytic agents than those of a higher soln. pressure. H. G.

**Further electrobiological studies.** K. KOSAKA AND M. SEKI. *Okayama Igakkwai Zasshi* No. 386, 22 pp., reprint(1922); *Physiol. Abstracts* 7, 219.—A study of the galvanotropic reactions of blood corpuscles and some bacteria under varying conditions

of  $pH$ , temp., etc. The influence of the elec. charge carried by bacteria on phagocytosis has also been examd. (Cf. C. A. 16, 3946 and preceding abstr.). H. G.

**Neutralization of the acids secreted by the kidneys.** L. AMBARD AND F. SCHMID. *Compt. rend. soc. biol.* 86, 844-6(1922); *Physiol. Abstracts* 7, 253.—The hypothesis is put forward that an increase of H ions in the renal cells, provided there is no  $NH_3$  present, leads to a lowering of the threshold for Na and K. Org. acids like  $\beta$ -hydroxybutyric, on account of their low dissoc., may thus appear in the urine to a large extent unneutralized. H. G.

**Relation between hemoglobin, cell count and cell volume in the venous blood of normal human subjects.** H. C. GRAM AND A. NORGAARD. *Arch. Intern. Med.* 31, 164-70(1923).—The blood of 10 normal men and 10 normal women was analyzed for hemoglobin and cell count and vol. (including white cells). The cell count varied from 4.854 to 5.911, av. 5.454 millions per cu. mm. in the men and from 4.360 to 5.054, av. 4.654 in the women. The cell vol. varied from 42.38 to 50.00, av. 46.34% in the men and from 38.81 to 43.00, av. 40.53% in the women. The hemoglobin, calcd. as 100% = 18.5% O<sub>2</sub>, varied from 96.38 to 118.0, av. 108.84% in the men and from 88.00 to 102.25, av. 94.45% in the women. Calcd. as 100% = 5 million corpuscles, the values were 95.62-117.26, av. 108.32%, and 87.49-101.68, av. 93.85%, resp. The max. deviation in the relation of color (hemoglobin content) to cell count was 10%. I. G.

**The lipoids in the human ovary.** FELIX V. MIKULICZ-RODECKI. *Arch. Gynäkol.* 116, 203-51(1922).—A study was made of the lipid content of the ovaries from 120 cases, ranging from the 3rd fetal month to the menopause; micro-chemical criteria were used. In the development and involution of a corpus luteum menstruationis first phosphatides and cerebrosides appear in the granulosa cells of the ripening follicles and in the corpus luteum, then cholesterol and cholesterol mixts., particularly cholesterol-cephalin mixts. There may be traces of neutral fat but on the day of menstruation there is an abrupt increase in neutral fat. In comparison with the corpus luteum menstruationis the corpus luteum graviditatis contains little lipid. The luteum cells contain for the most part very little lipid, but more in the first months of pregnancy than later. In the menopause the theca cells of the atresic follicles contain varying amts. of lipoids, including fatty acids and soaps as well as neutral fat. In view of the fact that the corpus luteum is an organ of internal secretion of importance only before and at the beginning of pregnancy, and that in animal experimentation lipid ext. of corpora lutea has an effect on the uterus and breast related to the changes produced by pregnancy, it is probable that the internal secretion contains the complex lipoids which increase in the corpus luteum menstruationis but decrease at the beginning of pregnancy. It is not possible at present to connect other lipoids of the ovary with an internal secretion. The small amts. of lipoids contg. N and P probably represent primary cell constituents. The larger masses of lipoids in the corpus luteum atreticum and canalicans, that consist mostly of neutral fats, fatty acids and soaps, must be regarded as the result of cell degeneration. HARRIET F. HOLMES

**A theory of the muscular contraction.** P. P. LAZAREV. *Bull. acad. sci. Russie* 1919, 215-22.—A mathematical study of a theory outlined by the author in *Arch. Sci. Inst. Moscow* 1918, No. 1-2, 127, and based upon exptl. investigations by Лопб. K and Na in the ionized state are thought to produce a change in the aggregate state of albumins during contraction, while Ca and Mg ions produce a reversed effect during rest. The total results of the chem. process are contained in albuminous substance A of concn. C being changed to the substance B under the influence of K and Na ions of concn. C<sub>1</sub>. This change is slowed down by the influence of Ca and Mg ions of the concn. C<sub>2</sub>. The new substance B of the concn. C<sub>1</sub> ties up a part of A by the reaction of its own disintegration, which lowers the formation velocity of B also. A part of

the substance  $B$  is removed by the activity of the cells. Therefore, one has for the substance  $A$ :  $-dC/dt = (\alpha'_1 C_1 - \alpha'_1 C_2)C + \alpha'_2(C_1)$ , and for the substance  $B$ :  $dC_1'/dt = (\alpha'_1 C_1 - \alpha'_2 C_2)C - \alpha'_3 C_1' - \alpha'_4$ , where  $\alpha'_2$  grows from 0 to a const.,  $\alpha'_3$  decreases from a certain initial const. to 0 and  $\alpha'_4$  very slowly increases from a certain small figure to a const. limit at large  $t$ 's. If the muscle is placed in a soln. of salts, it can be subjected to periodic vibrations in the case of:  $0 < (\alpha'_1 C_1 - \alpha'_2 C_2) < 4\alpha_2$ , and on the nearness of this variable magnitude to one of the limits depends either a non-damped excitation of the muscle with a non-damped variation of the concn.  $C$  of the period  $T = 2\pi/\sqrt{\alpha_2(\alpha'_1 C_1 - \alpha'_2 C_2)}$  (left limit), or a very shortly damped excitation. Where the action of the salt soln. is very short and the muscle is excited by an outside medium (elec. current),  $\alpha'_2$  and  $\alpha'_4$  become equal to 0, and the final state is given by:  $C = C_0 e^{-(\alpha'_1 C_1 - \alpha'_2 C_2)t}$ ,  $C_1' = [C_0(\alpha'_1 C_1 - \alpha'_2 C_2)/\alpha_2 - (\alpha'_1 C_1 - \alpha'_2 C_2)]/[e^{-(\alpha'_1 C_1 - \alpha'_2 C_2)t} - e^{-\alpha_2 t}]$ . The value of  $C$  decreases continuously, but this decrease is relatively small, while the changes of  $C_1'$  from 0 to the final state are comparatively large, and therefore inflict a defining action upon the surface tensions in the muscle. The isometric tension in the muscle (under non-work conditions) is proportional to this surface tension and, therefore, to the concn. of  $B$  ( $C_1'$ ). The isotonic tension (when work is being performed) can be obtained from the isometric value by multiplying it with  $(1 - S/S_0)/(1 - S_m/S_0)$ , where  $S_0$ ,  $S_m$ , and  $S$  represent the summary side surface of the muscular elements, resp., in the normal, the max. contraction and the momentary state.

M. G. KORSUNSKY

**The kinetics of the muscular excitation.** P. P. LAZAREV. *Bull. acad. sci. Russie* 1919, 1035-9.—That the process of muscular excitation is due primarily to a local accumulation of ions, which produce a change in the aggregate state of the muscular albumin mols., is confirmed by the exptl. investigations of Victor Henri (*Arch. Moscow Inst. Sci.* No. 1, 154-1(1918)). Smoluchowski developed the differential equations for the kinetics of coagulation of albuminous solns. under the action of electrolytes (*C. A.* 11, 3140), and L. intends to use in his further studies the integrated equation:  $n_1 = n_0 \alpha n_0 / (1 + \alpha n_0)^3$ , representing the concn. of the doubled mols. as a function of the initial concn. of the plain mols. and of the time of excitation, as giving the approx. measure of the intensity of excitation.

M. G. KORSUNSKY

**Urea in the blood of animals.** A. MARIE. *Ann. inst. Pasteur* 36, 820-9(1922).—The normal urea content of rabbit blood as detd. by the method of Fosse is 0.125-0.140 g. per l. Acute infections and the injection of adrenaline markedly increase this, values 7 times the normal occurring occasionally. When rabbit liver emulsion is allowed to autolyse 24 hrs. a certain amt. of urea is found. This is doubled if before the autolysis the emulsion is treated with adrenaline-HCl. Possibly the rises in urea content of the blood noted clinically following the administration of certain drugs are due to an excitation of the adrenals. Horses do not show so much susceptibility as rabbits to infection, in respect to variation in blood urea concn., various antitoxin sera showing normal values for the most part. Cf. *C. A.* 16, 3343.

E. R. LONG

**The action of certain digestive enzymes in producing gastric leucopenesis.** M. LOEPPER and G. MARCHAL. *Compt. rend. soc. biol.* 88, 77-8(1923).—Introduction of pepsin or trypsin into the stomach causes a migration of leucocytes into the gastric cavity (65-70% of these are polymorphs).

S. MORGULIS

**Normal creatinine level of the blood.** E. JEANBRAU and P. CRISTOL. *Compt. rend. soc. biol.* 88, 65-6(1923).—Normally the blood creatinine is 0.9 to 2.0 mg. per 100 cc. blood.

S. MORGULIS

**The relation between the hemoglobin content, number of cells and volume in the blood of normal individuals.** A. NORGAARD and H. C. GRAM. *Compt. rend. soc. biol.* 88,

107-8(1923); cf. *C. A.* 16, 939.—The blood hemoglobin (*Hb*) is detd. as a function of the number (*h*) and the vol. (*v*) of red cells, thus:  $Hb = k_1 h = k_2 v$ . From an examn. of 20 normal bloods from individuals of both sexes it has been established that  $k_1 = 20.11$  and  $k_2 = 2.34$ . S. MORGULIS

The glycogen content of liver and muscles of castrated animals., MARIE PARHON. *Compt. rend. soc. biol.* 87, 741-3(1922); cf. *C. A.* 16, 3942.—The glycogen content of 100 g. fresh liver or muscle in normal and castrated dogs (6 weeks after the operation) was 4.852 and 0.684 g., resp., in the former and 4.264 and 0.654 g. in the latter. In another series of expts. a year after operation the glycogen content of the liver in the normal dogs was 5.927 g. per 100 g. and only 3.006 g. in the castrated ones; likewise, the glycogen content of the muscles changed from 0.892 g. to 0.613 g. in the latter. These results are interpreted in the sense that the removal of the sex glands occasions a hypertrophy of the thyroid and hypophysis whereby the metabolism of carbohydrate is accelerated, and leads to a diminution in the glycogen reserves in the tissues. The slow onset of this change is due to the fact that the hypertrophy of the other glands of internal secretion requires time. S. MORGULIS

Peptic digestion. SHIN SHIMA. *J. Biochem. (Japan)* 2, 207-28(1923).—The effect of various ions has been studied by the following method. Mixts. of 7 cc. of a 1% soln. of ovalbumin (prepd. by mixing equal vols. of 2% dialyzed ovalbumin and 1% HCl), 2 cc. of the different salt solns. of varying degrees of concn., and 1 cc. gastric juice obtained from dogs with Pavlov stomachs were incubated at 38°. At definite intervals the undigested ovalbumin was pptd. with 1.5 cc. of a 10%  $\text{CCl}_3\text{COOH}$ , this amt. having been found to be sufficient to throw down all the protein without removing any proteoses. The non-coagulable N was detd. by Folin's method. The salts employed were:  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{Na citrate}$ ,  $\text{NaFe}(\text{CN})_6$ . The results of the expts. indicate that the optimum reaction for the activity of pure pepsin lies between  $p_H$  1.15 and 1.64 ( $p_H$  1.5 is the av.). The addition of multivalent anions accelerated while that of multivalent cations inhibited peptic digestion. The optimum temp. is about 40°. S. MORGULIS

An investigation of the urine of pregnant women. III. MISAO HONDA. *J. Biochem. (Japan)* 2, 351-9(1923).—The following substances were isolated and identified in urines of pregnant women: alanine, valine, isoleucine, leucine, phenylalanine, histidine, methylguanidine with some admixt. of dimethylguanidine, lysine, creatine and creatinine. S. MORGULIS

Uric acid compounds of human blood. CH.-O. GUILLAUMIN. *Compt. rend. soc. biol.* 88, 31-3(1923).—A general discussion. S. MORGULIS

Determination of the quantity of adrenaline secreted by the suprarenal capsule during splanchnic stimulation; calculation of the level of adrenalinemia thus produced. A. TOURNADE AND M. CHABROL. *Compt. rend. soc. biol.* 88, 6-7(1923).—By means of vessel anastomosis the blood from the right adrenal of a dog deprived of the left adrenal was directed into another dog that had been completely adrenalectomized before the expt. The blood pressure of the latter was recorded, then the splanchnic nerve of the first dog was stimulated and the effect of this on the blood pressure noted. When the normal pressure level has been reestablished, solns. of adrenaline were injected into the vein of the completely adrenalectomized animal until the blood pressure rose to the same height as before. The quantity of adrenaline which was required to bring about this result was taken as a measure of the adrenaline secretion from one adrenal under splanchnic stimulation. By this method it was detd. that stimulation with a weak faradic current for 1 min. liberated on the av. 0.05 mg. adrenaline from one adrenal and this amt. sufficed to raise the concn. in the blood by 1:10000000. S. MORGULIS

The partition of creatinine in the corpuscles and plasma of the blood. E. JEAN-

BRAU AND P. CRISTOL. *Compt. rend. soc. biol.* 88, 7-9(1923).—There is more creatinine in the red cells than in the plasma but the relationship between the 2 is not definite. The creatinine content of the plasma and serum is practically the same. S. M.

Duodenal tube: Role of the mechanical factor in the secretion of duodenal juice. DAMADE AND DE GRATILLY. *Compt. rend. soc. biol.* 88, 125-6(1923).—In the normal person, before breakfast, the presence of the duodenal tube in the intestine does not produce any qual. change in the juice. Such alterations are found only during the digestive process. S. MORGULIS

The sugar of the blood and of the cerebrospinal fluid. M. POLONOVSKI AND E. DUHOT. *Presse med.* 31, 60-2(1923); cf. *C. A.* 16, 3943.—By subjecting blood and cerebrospinal fluid to the same analytical technic, the removal of protein and of loosely combined sugar by pptn. with alc., evapn. *in vacuo* and repptn. with colloidal Fe, the authors demonstrate a much closer agreement and parallelism between the free sugar content of the two fluids in normal and in certain pathol. conditions. These results support their hypothesis of the existence of an osmotic equil. between the blood and the spinal fluid. W. A. PERLZWEIG

The rate of decline of milk secretion with the advance of the period of lactation. S. BRODY, A. C. RAGSDALE AND C. W. TURNER. *J. Gen. Physiol.* 5, 441-4(1923).—The course of decline of milk secretion with the advance of the period of lactation may be expressed by the equation of a monomol. chem. reaction. The % decline with the advance of the stage of lactation is const. The speed of the process is detd. by the concn. of a limiting substance. Data are given for Holstein, Guernsey, Jersey and scrub cows. C. H. RICHARDSON

The rate of growth of the dairy cow. II. Growth in weight after the age of two years. S. BRODY, A. C. RAGSDALE AND C. W. TURNER. *J. Gen. Physiol.* 5, 445-9(1923); cf. *C. A.* 15, 2477.—Data presented on growth by wt. from 2 to 17 yrs. (practically the entire duration of life) show that the rate declines in a non-cyclic manner. It follows the course of decline of a monomol. chem. reaction, i. e., the % decline in growth with age is const. C. H. RICHARDSON

Forms of uric acid in the blood. M. P. WEIL AND GUILLAUMIN. *Paris Medical* 12, 588(1922); *J. Am. Med. Assoc.* 80, 729.—The authors distinguish between the total uric acid of the blood and the free uric acid with its salts. The usual methods give only the value of the latter. The other part of the total uric acid consists of more or less complete remnants of nucleotides, some of which give some of the reactions of uric acid. In others, hydrolysis of the plasma after removal of albumin has to precede the reaction. Their detn. is still in the exptl. stage. The uric acid of the plasma belongs almost exclusively to the free group. The combined uric acid is practically limited to the corpuscles, which contain also some free uric acid. A method of detn. is also given. L. W. RIGGS

Maximum quantities of glycogenic reserve in the liver of dogs of different ages. MME. Z. GRUZEWSKA AND FAUKE-FRÉMET. *Compt. rend.* 175, 1237-40(1922); cf. *C. A.* 15, 3871.—Prolonged overfeeding of a ration of rice sugar and horse meat is supported by the liver only if the animal is young and vigorous. Hepatic cells, either with age or under unfavorable conditions, undergo a weakening of their glycogenic functions. In order to find the max. of glycogen in the liver of a dog with an appropriate diet, it is necessary to make the analysis before the animal has attained its initial wt. before its fast. L. W. RIGGS

Presence of the "alkaline tide." R. S. HUBBARD AND S. A. MUNFORD. *J. Am. Med. Assoc.* 80, 304-5(1923).—The conclusion that there is an alk. tide is based on 20 expts. with 19 subjects who did not show evidences of acidosis by clin. or lab. tests, and who were not receiving acid or alk. therapy. The urine of 24 hrs. was collected

in 7 portions. From 7 A. M. to 7 P. M. a specimen was taken every 2 hrs., and all voided between 7 P. M. and 7 A. M. was combined as a single specimen. Acidity was detd. by Folin's titration method and  $pH$  by the method of Marshall (cf. *C. A.* 16, 2171). The reaction was less acid during the forenoon and afternoon periods than it was in the morning, at night, or during the period when the noon meal was taken. Only 8 out of 142 samples gave  $pH$  greater than 7.0. A study of the av. values of the reactions, the hourly excretion of acid in these cases and of the times at which alk. or nearly alk. specimens of urine were voided shows that a reduced acidity following meals (known as the alk. tide) exists.

I. W. RIGGS

**Influence of the hydrogen-ion concentration on the blood vessels of mammalia.** EDGAR ATZLER AND GUNTHER LEHMANN. *Arch. ges. Physiol.* (Pflüger's) 197, 221-34 (1922); cf. *C. A.* 16, 2544, 2902.—The amt. of fluid in the vascular system of mammalia per unit of time was registered; the degree of vascular contraction is related to the H-ion concn. of the perfusion fluid. Diminished H-ion concn. leads to vascular contraction; increased H-ion concn. to dilatation. If the concn. is increased above a certain level further dilatation does not occur; on the contrary, at  $pH$  less than 4.5 constriction often results. The smallest  $pH$  difference detected by the vascular reaction was 0.21. When the perfusion fluids are strongly buffered the vessels are more susceptible to  $pH$  changes than when weakly buffered solus. are used.  $NH_4Cl$ , in high concns., causes constriction regardless of the H-ion concn. These reactions are also to be observed in animals whose central nervous system has been destroyed.

G. H. S.

**Formation of bile pigments.** FELIX ROSENTHAL AND EDUARD MELCHIOR. *Arch. expl. Path. Pharm.* 94, 28-51 (1922).—There is no conclusive proof that the reticulo-endothelial app., particularly the star cells of the liver, are the chief place for the formation of bile pigments in pigeons, nor do the Kupffer cells have an icterogenic function in  $AsH_3$  jaundice in birds. In the so-called collargol hockade hile appears in the urine within 2 hrs. after the administration of  $AsH_3$ . Intense satn. of the Kupffer cells with Ag does not inhibit the formation of bile pigments in pigeons. Nor does collargol retention by the Kupffer cells cause a significant modification in the biliverdin excretion in the feces, in hile pigment elimination through the bile ducts, or in the biliverdin of the urine and hilirubin of the blood in mechanical icterus of the pigeon. Mechanical icterus of the pigeon due to ligation of the bile ducts leads to a yellow (bilirubin) blood icterus and a green (biliverdin) icterus of urine and tissues. The threshold value of the urine for hile pigments is extremely low in birds; the feces show the green pigment but urobilin and urobilinogen are lacking, or occur only in traces. Ligation of the ducts never leads to a marked hilirubinemia, and the latter is related to, an exhaustion of the ability of the kidney to excrete the bile pigments.

G. H. SMITH

**Internal secretion of the ovaries, investigated by parabiosis.** NAOSHI GOTO. *Arch. expl. Path. Pharm.* 94, 124-8 (1922).—Parabiosis was effected in rats by joining them together by colostomy. Before joining, one of the rats had a double ovariectomy performed. It appears that under such circumstances there is some substance in the circulating blood which is absent, or present only in traces, in the blood of normal rats. This unknown substance passes over into the circulation of the normal rat and directly or indirectly reacts upon the ovaries and uterus of this animal, causing hypertrophy. The effect upon the ovary is considered primary, that upon the uterus secondary, since the union of two castrated females results within a few days in an atrophy of the uterus in both animals.

G. H. SMITH

**Influence of carbon dioxide on the vessels of cold-blooded animals.** ROBERT HERBST. *Arch. ges. Physiol.* (Pflüger's) 197, 568-73 (1923).—Perfusion expts. in frogs showed that changes in the  $pH$  due to  $CO_2$  have the same effect as do similar changes in the acidity caused by other acids.

G. H. SMITH

**Blood of domestic animals. IV. Coagulation time.** K. AMENDT. *Arch. ges. Physiol.* (Pflüger's) 197, 558-67(1923).—By means of the method described by Bürker the coagulation times in min. were detd. as follows: man, 5; swine, 3.5; dogs, 2.5; horses, 11.5; cattle, 6.5; sheep, 2.5; goats, 2.5; rabbits, 4; hens, 4.5; and pigeons, 1.6.

G. H. SMITH

**Action of defibrinated blood on the isolated mammalian heart.** G. v. HEUKING AND A. v. SZENT-GYÖRGYI. *Arch. ges. Physiol.* (Pflüger's) 197, 516-17(1923).—The effect of the defibrinated blood of an animal upon its own isolated heart resembles that of a toxic dose of adrenaline.

G. H. SMITH

**Erythrocyte sedimentation. Effect of irradiation with ultra-violet light.** RUDOLF MÖND. *Arch. ges. Physiol.* (Pflüger's) 197, 574-82(1923).—The sedimentation rates of erythrocytes in protein-contg. fluids are modified by irradiation of the fluids. Irradiation of solns. of serum globulin and albumin hastens sedimentation, while treatment of fibrinogen solns. delays the reaction. Irradiation of plasma may cause a change in rate in either direction. Change in sedimentation rate is paralleled by a change in negative charge of the red blood cells, and the effects of protein solns. upon sedimentation are associated with the isoelec. points and with stability. G. H. S.

**Erythrocyte sedimentation. Effect of heating and shaking protein solutions.** TOKUJIRO KANAI. *Arch. ges. Physiol.* (Pflüger's) 197, 583-98(1923).—Heating serum for several hrs. diminishes the sedimentation rate of erythrocytes; the higher the temp. of heating (36-42°) the greater the effect. If the serum is shaken during the heating the rate is not altered.

G. H. SMITH

**Buffer power of mammalian tissues.** EDGAR ATZLER AND GUNTHER LEHMANN. *Arch. ges. Physiol.* (Pflüger's) 197, 206-20(1922).—Rabbits were perfused with solns. varying in  $p_a$  and buffer values. The tissues decrease the H-ion concn. of the perfusion fluid. The process may be expressed by a formula resembling Newton's cooling formula. The consts. of the formula are dependent upon the buffer grade of the soln. and the buffering power of the tissues. Comparison of the buffer power of rabbits with that of frogs shows that the buffering power can be regarded as a measure of the magnitude of metabolism of the animal.

G. H. SMITH

**Agglutination of erythrocytes.** RICHARD LEY. *Arch. ges. Physiol.* (Pflüger's) 197, 599-610(1923).—The agglutination of red blood cells in blood fluids depends upon the condition of the elec. charge, or upon the dissociation of particular proteins, for in the presence of H-ion concns. of diff. degrees the erythrocytes show changes in agglutinability, just as the associated proteins, fibrinogen, globulin, and albumin show tendencies toward flocculation.

G. H. SMITH

**Penetrability of the lung for ammonia.** C. LILJESTRAND, C. DE LIND VAN WIJNGAARDEN, AND R. MAGNUS. *Arch. ges. Physiol.* (Pflüger's) 196, 247-74(1922).—The  $CO_2$  tension of the alveolar air in artificially perfused surviving isolated lung isf 0.8-2.1 mm. Hg, only a little higher than in the room air (0.6 mm.). The  $CO_2$  content of the blood is 2.3-8 vol. %. This small amt. of  $CO_2$  can hinder but little the excretion of  $NH_3$ . When the artificially perfused lung inhales air contg.  $NH_3$  in amts. of 0.001-0.004% a considerable percentage of the  $NH_3$  (13 to 42%) is found in the blood. With an  $NH_3$  content of the perfusion blood of 0.012-0.018% the  $NH_3$  is given off from the pleural surface of the lung. The detection of  $NH_3$  in the expired air depends upon the method used, but with proper precautions to guard against loss  $NH_3$  can be detected when the blood has a concn. of only 0.012%. With 5 to 6% of  $CO_2$  in the alveolar air the  $NH_3$  elimination through the lung is materially diminished; so that with less than 0.02% of  $NH_3$  in the blood no  $NH_3$  can be detected in the expired air. The alveolar epithelium is permeable for  $NH_3$  in both directions.

G. H. SMITH

**Hibernation and its modification by endocrine-gland extracts.** PAUL SCHENK.



*Arch. ges. Physiol.* (Pflüger's) 197, 66-80(1922).—Metabolism expts. upon hibernating hedgehogs in the Haldane-Gürber app. showed that in deeply lethargic animals the respiratory quotient varied between 0.41 and 0.65. The  $\text{CO}_2$  elimination equalled 14.49-84.16 mg. per kg. of body wt. per hr.; the O utilization amounted to 20.29-97.59 mg. The decline in wt. per kg. of body wt. varied between 2.12 and 3.66 g. in 24 hrs. The subcutaneous injection of thyroid, thymus, hypophysis, and adrenal exts. very strongly increased the metabolism. Thyroid was most effective. The respiratory quotient increased, during the hr. following the injection, to 0.68-0.83. The amt. of eliminated  $\text{CO}_2$  during the waking was 1900-2200 mg. per kg. of body wt. per hr.; about 1600-2100 mg. of O was used. Hibernation is the result of hypofunction of the glands of internal secretion induced by temp. changes in the external environment.

G. H. SMITH

Effect on blood pressure and the non-protein nitrogen in the blood of excessive fluid intake. J. L. MILLER AND J. L. WILLIAMS. *Am. J. Med. Sci.* 161, 327-34(1921).—The ingestion of large amts. of fluid causes a marked increase in blood pressure (systolic, from 200 to 242; diastolic, from 104 to 140) in patients with hypertension. The promptness with which the kidneys excrete the fluid detrs. the effect. The urea N of the blood was not affected; in some cases the uric acid of the blood was diminished.

G. H. SMITH

Influence of thyroid on heat regulation. GERTY CORI. *Arch. expil. Path. Pharmacol.* 95, 378-80(1922).—Schenk (*C. A.* 16, 2724) failed to mention that the author has presented data bearing upon the heat restoration curves following the cooling of rabbits which had suffered the removal of the thyroid.

G. H. SMITH

Blood platelets of mammals. L. RIESS. *Arch. expil. Path. Pharmacol.* 90, 318-29(1921).—The structure of the blood platelets and their parallelism with the no. of leucocytes favor a genetic relationship between the two types of cells. Chemically, the platelets and the leucocytes show analogous substances in their compn. Physiologically, the platelets play a role in coagulation and in the formation of thrombin.

G. H. SMITH

#### G—PATHOLOGY

H. GIDEON WELLS

Periodic variations in basal metabolism rate in tuberculous women. P. H. PIERSON. *Am. Rev. Tuberculosis* 6, 1046-52(1922).—The study was made on 5 afebrile tuberculous patients and 1 non-tuberculous chronic bronchitis patient whose condition was worse at the menstrual period. There seems to be a menstrual or premenstrual rise in the basal metabolic rate in tuberculous women followed by a fall in the post-menstrual period. This variation may explain some of the difference of opinion as to the basal metabolic rate in tuberculosis and should be taken into account when figures are presented regarding this lab. aid. There is added evidence that the thyroid or several endocrine glands are involved in the ability of an individual, or a family, to resist tuberculosis.

H. J. CORNER

An experimental study on the behavior of extravasated blood in the lungs. H. J. CORPER, O. S. KRETSCHMER AND MAX B. LURIE. *Am. Rev. Tuberculosis* 6, 1100-13(1923).—Normal unclotted blood injected intratracheally into rabbits is rapidly aspirated into the finer air divisions where it is retained and induces a proliferative reaction on the part of the pulmonary tissues. Pigmentary changes and disappearance of the blood are complete in 1-4 weeks, but there still remains an induration at the site of localization of the blood due to the proliferative pneumonitis induced by the blood, which may in cases persist longer than 4 weeks. Contrary to the generally accepted idea, a large amt. of the intratracheally injected blood is retained in the lungs of rabbits

in conformity with studies by Mullin and Ryder (*Am. Rev. Tuberculosis* 6, 683(1920) and Corper (*J. Am. Med. Assoc.* 78, 1858(1922); 79, 1739(1922); and *Am. Rev. Tuberculosis* 6, 813(1922)). Normal unclotted blood, which has been injected into the pleural or peritoneal cavities of rabbits, undergoes a defibrination within a short period of time (less than 1 hr.) with the formation of very fine fibrin networks upon the pleural and peritoneal surfaces. The blood withdrawn from the pleural or peritoneal cavity is of approx. normal Ca content and has suffered no apparent changes save those due to the defibrination during its residence in these body cavities, conforming with Denny and Minot (*C. A.* 10, 1198) and Henschen, Herzfeld and Klinger (*Beitr. Klin. Chir.* 104, 196(1917)), and due to agitation by visceral movements, the speed of coagulation being dictd. by the rate of agitation. H. J. CORPER

Further studies on the complement-fixation reaction as applied to tuberculosis. J. D. ARONSON AND P. A. LEWIS. *Am. Rev. Tuberculosis* 6, 1024-34(1923).—No evidence was found of more than one antigenic substance, and this is found in acceptable form in several preps. Petroff's glycerol ext., Besredka's antigen, the alc. ext. used by Craig, the simple suspension of living tubercle bacilli and doubtless the "autolyzate" of Corper are of essentially equal worth. The alc. ext. and the glycerol ext. are the easiest to prep. and keep, the alc. ext. being superior in the latter respect. The most important feature of the reaction is that the time of primary incubation is longer than that in the classical Wassermann reaction (2-4 hrs. as against 30 min.) The longer time is necessary to secure comparable results with the bacillary suspension which becomes less practical on this account, as well as by reason of its limited keeping qualities. The application of the reaction in practice is limited by the fact that about 10% of clinically normal persons give a positive reaction. This is not materially different with any antigen. With an immune goat serum of high potency, as a tentative standard, and under favorable conditions the reaction is const. and reliable. Antigenic substances in the body fluids and tissues of tuberculous animals obtained by extn. with alc. could not be demonstrated. H. J. CORPER

Resistance to experimental peritoneal tuberculosis following oil injections. W. F. PETERSEN AND S. A. LEVINSON. *Am. Rev. Tuberculosis* 6, 1035-9(1923).—Inasmuch as liquid petrolatum seems as effective as the animal or vegetable oils used, the effect is probably due to the mild peritoneal irritation brought about by the oils which can be demonstrated by histological examination. H. J. CORPER

An attempt to differentiate human and bovine tubercle bacilli by means of the anaphylactic reaction. H. J. CORPER AND SALING SIMON. *Am. Rev. Tuberculosis* 6, 1087-90(1923).—The symptoms obtained in tuberculous guinea pigs (infected subcutaneously) were identical to those obtained in normal animals given intraperitoneal injections of living tubercle bacilli (0.001 to 1.0 g.). In no case was a typical acute anaphylactic react seen, such as occurs with sol. proteins. In larger doses (1.0 g.) living tubercle bacilli as well as dead (heat-killed) bacilli, given intraperitoneally, were profoundly toxic, producing an acute and early death of the guinea pig. A correlation was noted between the toxicity of the living tubercle bacilli injected intraperitoneally and the amnt. of generalized tuberculous involvement at the time. No strain specificity was noted. The virulence was also of no significance. Dead human or bovine tubercle bacilli injected subcutaneously into guinea pigs did not act as antigens for the general anaphylaxis reaction to second intraperitoneal injections of living or dead virulent human tubercle bacilli given 25 days later. The anaphylaxis reaction in guinea pigs is not suited to differentiate various strains of human and bovine tubercle bacilli. H. J. CORPER

The auto-urine reaction of Prof. Wildbolz. HEDWIG KUHN. *Beitr. Klin. Tuberkulose* 51, 24-31(1922).—The auto-urine reaction was tried in 154 cases of tubercu-

losis (pulmonary in all stages 128, glandular 15, bone 9, kidney 1 and tuberculous peritonitis 1), 7 non-tuberculous patients and 11 normal individuals. Of 26 clinically active cases 14 were positive and 5 weakly positive; of 25 moderately active cases 16 were positive and 4 faintly so; of 58 slightly active cases 28 were positive and 15 faintly so; of 30 clinically questionably active 7 were positive and 5 weakly so; while of 13 clinically inactive cases, 1 was faintly positive; of the clinically non-tuberculous and normal cases 2 were positive and 2 weakly so. The Wildbolz reaction agreed with the tuberculin reaction in 110 of 142 cases (77%), disagreed in 16 cases (11%) and was questionable in 16 cases (11%). Of 35 reinoculated cases 11 (31%) did not give the expected results. The findings are too uncertain to allow a differential diagnosis between an active and inactive process. The original should be consulted for detailed data.

H. J. CORPER

**Chondroituria in amyloidosis of the kidneys.** KARL DIETL. *Beitr. klin. Tuberkulose* 51, 18-23(1922).—Degenerative processes in the kidneys are not ordinarily revealed by the usual albumin tests and only in amyloidosis, which goes hand in hand with fatty degeneration of the kidney parenchyma, are larger amts. of albumin found. The views of Fischer that in the majority of cases of chronic pulmonary tuberculosis mild albuminuria obtains could not be verified. In severe cases of phthisis there was found, on the other hand, acetic acid derivs. (according to Strauss attributable to disturbances in the tubules) and more frequently chondroitinsulfuric acid (according to Pollitzer an index of glomerular injury). Amyloid is a chondroitin-albumin combination pptd. in the tissues in insol. form. The slight turbidity occurring in normal urine upon the addition of acetic acid is, according to Mörrer, a chondroitinsulfuric acid-albumin combination; this substance is increased in pathological urines. The reaction occurring is the result of the liberation of the chondroitinic acid and this ppts. the albumin. Chondroitinsulfuric acid is detd. by adding horse serum to the acetic-acid-treated urine. According to Leupold the amyloid formation in chronic pus conditions is based on disturbances in the  $H_2SO_4$  metabolism; the same processes according to Hansen also increase the chondroitinsulfuric acid. Amyloidosis is found mainly with tuberculous processes, in phthisis when the intestines are involved or when mixed infections occur. Chondroituria precedes albuminuria in these conditions.

H. J. CORPER

**The urochromogen reaction curve and its significance in pulmonary tuberculosis.** ALFRED GOTTSCHALK. *Beitr. klin. Tuberkulose* 51, 1-11(1922).—The urochromogen curve extending over a period of time and performed by the crude quant. Moeller modification (*Med. Klin.* 1921, No. 8, 228) is, in comparison to the single detn., a valuable aid for differentiating the form, and judging the prognosis of pulmonary tuberculosis. The fibroid or cirrhotic nodose (productive), febrile or subfebrile, prognostically favorable phthisis cases present a negative or, only rarely, a weakly positive urochromogen reaction, while predominantly exudative, cavernous, febrile cases of phthisis of unfavorable prognosis give a definite, and, in advanced cases, a strongly positive reaction. The urochromogen reaction is far more sensitive and when definitely positive appears earlier and more regularly in severe pulmonary tuberculosis than the diazo reaction.

H. J. CORPER

**The immunity condition as a basis for artificial immunization in the prevention and treatment of tuberculosis.** HEINRICH RIECKENBERG. *Beitr. klin. Tuberkulose* 51, 146-9(1922).—Holländer (*Z. Tuberk.* 32, No. 5; 35, No. 2) reported on serological and Pirquet reaction studies on the basis of which it was possible to det. the natural protection against tuberculosis, and in patients det. the prognosis. The protection was inherited and not artificially developed. 0.5 cc. undil. serum of the patient is superimposed by 0.5 cc. of a tuberculin-carbol-salt soln.(10% tuberculin, 0.5% phenol

and 0.85% NaCl). In positive cases a contact ppt. ring occurs after 24 hrs.' incubation. Holländer did not utilize controls. Rieckenberg used several tuberculins and found irregular results which dispute the clinical value of the test. Ring formation occurred in tuberculin-free controls. Different tuberculins gave irregular results. Tests at 4 weekly intervals also proved inconsistent. The ppts. are probably of non-specific nature. Clinically the findings did not agree with Holländer's prognostic index.

H. J. CORPER

**Sulfhemoglobinemia.** V. R. MASON AND F. D. CONROY. *Bull. Johns Hopkins Hosp.* 32, 391-4(1921); *Physiol. Abstracts* 7, 136.—Some cases of intense persistent cyanosis are due to sulfhemoglobin formation, and there is some evidence that sulfides formed in the bowel gain access to the blood.

H. G.

**Diastase content of urine in mental disorders.** E. GOODALL AND H. A. SCHOLBERG. *J. Ment. Sci.* 68, 1-5(1922); *Physiol. Abstracts* 7, 124.—120 cases of various diseases in asylums gave no evidence of pancreatic disease as indicated by the urinary-diastase test.

H. G.

**Cholesterol of the blood.** C. ALESSANDRI. *Riforma Med.* 37, 1095(1921); *Physiol. Abstracts* 7, 104.—Cholesterol contents of the blood in 22 patients suffering from various diseases are given. In 10 cases the cholesterol content was found to be increased half an hour after adrenaline administration, subcutaneous or intravenous. Adrenaline seemed to mobilize cholesterol deposits.

H. G.

**The relation of blood coagulation to purpura and hemophilia.** H. W. C. VINES. *Med. Sci.* 5, 496-502(1922); *Physiol. Abstracts* 7, 103.—The primary agent in blood coagulation is lysis of platelets. The retractility of blood clots is dependent on platelets. Evidence is cited to show that purpura constitutes a failure of coagulation in which there is a deficiency of platelets, but without lack of substances essential to clotting. The opinion of Duke is mentioned that the coagulative agent, thrombokinase, usually derived from platelets, is present in a form which precludes a sufficiently rapid union with Ca salts. In hemophilia the platelets and bleeding time are usually normal, but the coagulation time is delayed. There is a quant. lack of thrombokinase, as contrasted with a qual. deficiency in purpura. The physiol. aspects of the treatment of the hypercoagulability of the blood associated with an anaphylactic condition are discussed. The increased coagulability following the application of X-rays to the spleen and liver is assigned to a deficiency of the primary clotting agent of the blood. The view of Mills is accepted that the agent initiating coagulation is probably an adsorption aggregate formed of a phospholipoid, a protein, and Ca. The possibility of hemorrhagic conditions arising from a deficiency of Ca is reviewed. It is urged that the majority of hemorrhagic states are dependent on a deficiency, either quant. or qual., in the lipoids of the blood. The points of agreement and of disagreement in the theories of coagulation of Morawitz, Howell, Gratia, and of Bordet and Delange are brought out. The increasing complexity and "perhaps decreasing probability" of Howell's views are commented on. The recent conclusion of Mills and Guest that the lipid and Ca in tissue coagulins unite directly with blood fibrinogen and so enter into the formation of fibrin is rejected, while of current hypotheses that of Bordet and Delange is regarded as the most probable.

H. G.

**Cholesterol content of blood in kidney diseases.** A. HAHN AND E. WOLFF. *Z. klin. Med.* 92, 393-405(1921); *Physiol. Abstracts* 7, 123.—Increase of cholesterol in the blood is only found with tubular nephritis, and does not run parallel with the retention of N and high blood pressure. The increase is the highest in the serum, and cholesterol and cholesterol esters participate nearly in the same relation. In the red blood corpuscles there is also an increase of cholesterol and fairly large quantities of cholesterol esters.

H. G.

Content of serum proteins after serum injections. W. BERGER. *Schweiz. med. Woch.* 52, 225-8(1922); *Physiol. Abstracts* 7, 176.—See C. A. 17, 415. H. G.

A complement-fixation test in coccidiosis of the rabbit. S. W. PATTERSON. *Brit. J. Exptl. Pathol.* 4, 1-4(1923).—Antigens were prepd., best by extg. the infected liver with carbolized normal saline soln. HARRIET F. HOLMES

Testing the antigenic value of diphtheria toxin-antitoxin mixtures. A. T. GLENNY, K. ALLEN AND BARBARA E. HOPKINS. *Brit. J. Exptl. Pathol.* 4, 19-27(1923).—The toxicity test alone may give incomplete or erroneous conclusions as to the immunizing value of a toxin-antitoxin mixt. intended for immunization against diphtheria. Four methods are described for testing the antigenic value of mixts.: (a) Tracing the antitoxic value of the blood of rabbits after a single subcutaneous injection of the mixt. as a "primary stimulus." (b) Accelerating the results of (a) by a subsequent injection, as a "secondary stimulus," of either the same mixt. or of a Schick dose of toxin. (c) Tracing the increase in antitoxic values of the blood of immune rabbits after a subcutaneous injection of the mixt. as a secondary stimulus. (d) Injecting guinea pigs, which have survived the test for toxicity of the mixt., with Schick doses of diphtheria toxin at weekly intervals commencing 3 weeks after the injections of the mixts. HARRIET F. HOLMES

Concerning the formaldehyde-gel reaction in the diagnosis of syphilis. R. A. KILDUFFE. *J. Lab. Clin. Med.* 8, 409-11(1923).—The technic of Gate and Papacostas was used. Two drops of 40% formalin were added to 1 cc. clear serum, and the tube was incubated 24 hrs. The formation of a clear jelly-like clot was considered a positive reaction. In 480 cases this reaction gave many negative results in syphilis and many positives in the absence of syphilis, as controlled by the Wassermann reaction. E. R. LONG

The mediation of hemolytic serum action and complement activation. Investigations with inulin and B. prodigiosus. SHIGO KONDO. *Z. Immunitäts.* 36, 76-96(1923).—Confirming Sachs and Stilling (C. A. 14, 2024) K. found that inulin suspension but not inulin soln. mediated the hemolytic action of guinea pig serum without further addition of amboceptor. Confirming Ritz and Sachs (C. A. 14, 1378) he found the anticomplementary action of prodigiosus bacilli usually independent of the amt. of guinea pig serum. Young cultures were occasionally anticomplementary when the amt. of guinea pig serum was decreased. Suspensions of bacilli could be hemolytic, the red bacilli grown at room temp. more so than the white variety grown in the incubator, the optimum hemolytic action occurring with young cultures. Occasionally bacilli heated to 55° showed slight hemolytic action. Guinea pig serum inhibited the hemolytic action of suspensions of the bacilli. A proteus bacillus (X 19), which was like prodigiosus in its hemolytic action, unlike prodigiosus was the more anticomplementary the smaller the amts. of guinea pig serum which were used with it. E. R. LONG

Complement in malaria. ALEX. RADOSAVLJEVIC. *Z. Immunitäts.* 35, 429-46(1923).—The complement content of the blood is decreased in malaria. This is in such sharp contrast with the situation in other diseases, where complement is usually increased, as to have diagnostic value. The lowering of the complement is the result of a prepatoxysmal injury of complement coincident with the prepatoxysmal hemoclastic crisis, and is caused by the decompn. products of plasmodia and erythrocytes in the blood. E. R. LONG

The recognition of saponin hemolysis. A. LUGER, W. WEIS-OSBORN AND O. EHRENTZL. *Z. Immunitäts.* 36, 17-33(1923).—Lecithin emulsions contg. a high concn. of lecithin inhibit the hemolytic action of saponin; concns. of middle degree promote it, while low concns. are without influence. Carcinoma sera inhibit saponin hemolysis

less than normal serums or serums in most other diseases, probably because of their lower cholesterol content. A certain % of serums in pregnancy does not show an inhibition of hemolysis corresponding to their cholesterol content. E. R. LONG

The theoretical value of investigations on serum protein fractions for the Wassermann reaction. H. OELLER AND M. SCHIERGE. *Z. Immunitäts.* 36, 59-67(1923).—A discussion. The protein fractions of serum cannot be sharply sepd. The same conditions are not followed by different authors in their prepn. There are great difficulties in assigning complement-binding activity to a definite fraction. E. R. LONG

The type specificity of antibodies. J. I. KRITSCHESKY. *Z. Immunitäts.* 36, 1-16(1923).—Sheep erythrocytes possess heterogenic chicken erythrocyte antigen, which can be demonstrated by the development of hemolysins in rabbit immunization. Horse kidney also contains heterogenic chicken antigen. E. R. LONG

The theory of the gold-sol and mastix reaction. KARL PRESSER AND ALFRED WEINTRAUB. *Z. Immunitäts.* 36, 34-58(1923); cf. *C. A.* 16, 3099.—In the gold-sol reaction globulins prepd. from sera or body fluids are able to call forth the flocculation reaction characteristic for pathologic fluids only within a certain range of concn. This flocculation, maximal at first, becomes weaker with decreasing concn. and finally ceases. In the mastix reaction these globulins show maximal flocculation from the highest concn. to the limits of their activity. There is no difference in the action of globulins prepd. from Wassermann-positive and Wassermann-negative sera. Albumins by themselves cause no changes in the gold-sol reaction; they protect gold sol from electrolyte flocculation and inhibit flocculation by globulins. In the mastix reaction albumins in high concn. inhibit the NaCl flocculation; in low concn. (0.06%) they are themselves feebly active. In this reaction globulins hinder globulin flocculation only when in high concn. The so-called luetic curves can be imitated in the gold-sol and mastix reactions with mixts. of albumins and globulins in certain proportions. Albumins and globulins prepd. from Wassermann-positive and -negative sera show no difference in this respect. Meningitis curves can be similarly imitated, completely in the mastix reaction, partially in the gold-sol reaction. E. R. LONG

The prophylactic action of atropine sulfate upon the anaphylactic and allergic reactions of the excised uterus of virgin guinea pigs. O. O. STOLAND AND N. P. SHERWOOD. *J. Immunol.* 8, 91-173(1923).—Doses of atropine, from 1 to 4 cc. of a 1% soln. added to 25 cc. of Tyrode's soln., prevent the action of otherwise reactive doses of an antigen when applied to the horns of the uterus of a virgin guinea pig. Smaller doses of atropine produce an increase in the tone of the uterus muscle, but larger doses inhibit spontaneous contractions or decrease the tone slightly. Pituiratin added to the soln. invariably results in contraction following the administration of atropine; therefore the uterus muscle is not paralyzed. It is suggested that antigens act upon the same mechanism in the neuromuscular complex as does pilocarpine; their action is, therefore, neutralized by atropine. The myoneural junction is believed to play an important role in the sp. response of uterine strips from sensitized virgin guinea pigs. E. R. LONG

The complement-fixation test in chronic gonorrhea in women. M. A. WILSON, MARY V. FORBES AND FLORENCE SCHWARTZ. *J. Immunol.* 8, 105-20(1923).—Individual guinea pig serums must be tested for fixability with known gonococcus antibody plus gonococcus antigen before they can be used as complement for tests of patients' serums. The negative results with control human serums in the series studied indicate that the gonococcus complement-fixation test is sp. E. R. LONG

Hepatic reactions in anaphylaxis. II. The hepatic mechanical factor in peptone shock. W. H. MANWARING, SELLING BRILL AND W. H. BOYD. *J. Immunol.* 8, 121-30(1923); cf. *C. A.* 17, 1068.—The increased resistance to hepatic blood flow cannot be

regarded as a major factor in peptone shock. The portal blood pressure increases about 7 mm. Hg during the first 45 sec. of peptone shock, and then gradually falls, reaching normal in 8-12 min. Perfusions of isolated livers show an increased resistance to perfusion flow as a result of the action of peptone or peptone-blood mixts.; this reaches a max. during the 2nd min., and then gradually decreases, being restored to approx. normal by the 10th min. Mechanically increased resistance to hepatic out-flow sufficient to raise portal blood pressure 10 mm. Hg, the max. rise during peptone shock, does not cause the hepatic-intestinal cyanosis characteristic of peptone shock, nor the characteristic fall in carotid blood pressure. III. **Extrahepatic mechanical reactions in peptone shock.** W. H. MANWAKING AND W. H. BOYD. *Ibid* 131-9.—Unneutralized Witte peptone, tested by perfusion methods on isolated canine tissues, gives mechanical reactions in the following parts: isolated liver, marked increase in perfusion resistance, reaching its max. in 1 min., with partial or complete recovery in 8 min.; isolated lungs, reactions similar to those in the liver but more pronounced, with practically no tendency to recovery by the end of 8 min.; isolated intestines, slight decrease in perfusion resistance, reaching its max. in 1 min., with partial recovery by the end of 8 min.; isolated hind quarters, reactions similar to those of the isolated intestines, but with less tendency to recovery by the end of 8 min.; isolated heart, reactions intermediary between those of the isolated liver and isolated hind quarters. The combined effect of these mechanical reactions is conceivably sufficient to account for the characteristic clinical picture of peptone shock. E. R. LONG

A substance in immune horse serum which interferes with alexin fixation. HANS ZINSSER AND JULIA T. PARKER. *J. Immunol.* 8, 151-61(1923).—Certain antipneumococcus horse sera, although showing powerful pptn. reactions with pneumococcus antigen, do not sensitize similar antigens to alexin fixation. Such sera also will prevent alexin fixation when added in small amts. to tubes of antipneumococcus antigen sensitized with antipneumococcus rabbit serum under conditions which ordinarily would give a positive reaction. In order to obtain this interfering action it is necessary to add the horse serum to the sensitized antigen before the alexin. If the alexin is added first and given 30 min. at 37.5° subsequent addition of the horse serum does not interfere with the fixation. The interfering effect of the horse serum can be removed by absorbing with sensitized pneumococci. E. R. LONG

**Bacterial anaphylaxis.** N. P. SHERWOOD AND O. O. STOLAND. *J. Immunol.* 8, 141-50(1923).—Active or passive sensitization against bacterial protein of *B. typhosus*, *paratyphosus* B or *B. enteritidis* is not demonstrable by the smooth muscle reaction of Schultz and Dale. In a small number of animals suspensions of the bacteria mentioned and *B. coli* stimulated the inhibitory mechanism of intestinal loops or uterine horns. In the rabbit this is shown by a drop in tone and loss of contractility, and in the guinea pig by drop in tone. Suspensions of other bacteria and of sol. proteins either stimulated the accelerating mechanism or had no effect. E. R. LONG

**The Ehrlich aldehyde reaction.** E. ISNARD. *Compt. rend. soc. biol.* 88, 16-8 (1923).—The Ehrlich aldehyde reaction is not definitely indicative of any pathological condition. Even in typhoid fever, where it has been proposed as a special test, not infrequently, negative results are produced. S. MORGULIS

Variations in the  $pH$  of serum following intravenous injections and repeated injections of heterogeneous proteins. P. MENDELEEFF. *Compt. rend. soc. biol.* 88, 146-8 (1923).—Intravenous injections of heterogeneous proteins—milk, serum—into the young animal always occasion changes in the  $pH$  of the serum. By repeated injections the  $pH$  of the serum is brought back to normal and is no longer affected by new injections. S. MORGULIS

**Effect of thyroïdin treatment on the basal metabolism of two cases of myxedema**

of the congenital type. H. HERMANN AND E. ABEL. *Compt. rend. soc. biol.* **85**, 93-5 (1923).—Under the influence of thyroïdin treatment the basal metabolism of two myxedematous girls—18 and 22 years old—soon increased and surpassed the normal for their age. From a subnormal level of 26.9 and 12 Cal. it rose to 55 and 57.9 Cal., which is the metabolic rate of children between the ages of 5 and 10 years. S. M.

Basal metabolism of the obese. MARCEL LABBÉ AND HENRI STÉVENIN. *Compt. rend. soc. biol.* **88**, 9-12(1923).—The basal metabolism was detd. in 46 cases of obesity with the following results: 58.6% showed a normal rate of metabolism, 13.4% a higher metabolism and 28% a lower metabolism than normal. In the first group were individuals whose obesity was definitely due to a sedentary life with an overabundance of food; these responded well to a simple dietary restriction. In the second group there were at least several with frank symptoms of hyperthyroidism, which was atypical insofar as it was associated with obesity. The 3rd group with a basal metabolism below normal had several individuals which were clearly myxedematous or of the adiposogenital type. This group responded well to treatment with thyroïdin. The use of thyroïdin in the first 2 groups is either contraindicated or will be of no benefit.

S. MORGULIS

Hypercholesteremia in the aged. C. J. PARHON AND MARIE PARHON. *Compt. rend. soc. biol.* **88**, 231-3(1923).—In all subjects examd. those of over 70 yrs. of age showed a definite increase in the cholesterol content of the blood. S. MORGULIS

Researches on the secretory function of the pancreas in hypopeptic dyspepsias. M. GAROFEANO. *Compt. rend. soc. biol.* **88**, 233-5(1923).—Both the amylase and the trypsin are 1.5 to 3 times as great in the pancreatic juice from dyspeptics as in normal juice. The more serious the disturbance of the peptic secretion the greater is the compensatory increase in the enzyme content of the pancreatic secretion. S. MORGULIS

Determination of cholesterol in therapeutic serums. A. MARIE. *Compt. rend. soc. biol.* **88**, 76-7(1923).—In horses which were subjected to a prolonged action of large quantities of bacterial cultures and of their toxic products the cholesterol content of the blood was invariably below normal (0.4 g. per l.). S. MORGULIS

Serological studies on hemoglobin with special regard to the consideration of the practical application of the "hemoglobin precipitin." SHIGEO HIGASHI. *J. Biochem.* (Japan) **2**, 315-39(1923).—Pure hemoglobin, when it is introduced into the organism, gives rise to precipitins, complement-binding antibodies and anaphylactic antibodies. The statement that it also functions as lysinogen and agglutinin is considered erroneous. The hemoglobin has a certain degree of species specificity and at the same time a very marked organ specificity. In the biol. reactions of hemoglobin the relation between the organisms comes clearly to view; thus, a human hemoglobin antiserum gives a definite reaction also with ape hemoglobin solns. Similar relation was found between hemoglobin of sheep, goat and ox, also between that of hens, ducks, pigeons and sparrows. In spite of such close relation it is nevertheless possible through special immunization expts. to differentiate the hemoglobin of very near relatives. Klein's erythroprecipitins are in all probability also due to the presence of hemoglobin precipitin but contaminated with hemolysin and agglutinins which are not found when the immunization is made with pure hemoglobin. In view of the specificity of the hemoglobin precipitin reaction H. considers this as a new biological reaction available for the forensic examn. of blood.

S. MORGULIS

Anaphylaxis. IV. Refractive power of sera before and after an initial and a second injection of heterologous protein. EMIL ADBERHALDEN AND ERNST WERTHEIMER. *Arch. ges. Physiol.* (Pflüger's) **197**, 85-9(1922).—Polarimeter, refractometer and interferometer readings, resp., upon rabbit sera were: before sensitizing injection of heterologous protein—0.65°, 1483, 52.8; 24 hrs. after sensitizing injection—0.64, 1507,



53.7; before intoxicating injection—0.64, 1586, 56.3; after intoxicating injection—0.64, 1689, 58.6. The reaction following the intoxicating injection is qual. the same as that following the sensitizing injection; it differs only in degree. G. H. SMITH

**Different hemagglutination reactions in jaundice cases and their significance.** JOSEF VORSCHÜTZ. *Arch. expl. Path. Pharmacol.* 95, 235-7(1922).—The relation of the globulin and  $P_2O_5$  content of the serum to the sedimentation of red cells in icterus is discussed. Jaundice cases show considerable variation in serum properties.

G. H. SMITH

**The effects of chloroform narcosis upon the growth of transplanted animal tumors.** T. KIMURA, K. OHBA AND Y. WADA. *Gann (Japan. J. Cancer Res.)* 16, 19-22(1922).—Repeated anesthesia and lactic acid injections failed to increase rate of growth of transplanted tumors in rats.

H. G. WELLS

**The effects of lanolin feeding upon the growth of transplanted chicken chondroma.** N. AKAMATSU. *Gann (Japan. J. Cancer Res.)* 16, 30-2(1922).—A marked acceleration in growth of transplanted tumors was observed in fowls fed lanolin and the tumors were more atypical.

H. G. WELLS

**The meaning of serum globulin in luetic reactions.** KIYOWO TAOKA. *Kilasato Arch. Exptl. Med.* 5, 44-61(1922).—Pptn. of globulin by 33% satd.  $(NH_4)_2SO_4$  soln. removes the reactive substance from syphilitic serum. Partial removal of the globulin augments the Sachs-Georgi reaction. Heating serum at  $56^\circ$  for  $1/2$  hour weakens the Wassermann reaction but increases the S.-G. reaction. Serum globulin from either normal or syphilitic serum has an anticomplementary effect in the W. reaction which is removed by heating. Heating of the serum reduces the number of non-specific W. reactions, and increases the delicacy of the S.-G. reaction and, therefore, only such heated sera should be used.

H. G. WELLS

**Experimental investigation on antibody formation against transplantable mouse carcinoma.** I. K. YAMAGIWA AND T. KIMURA. *Gann (Japan. J. Cancer Res.)* 16, 1-11(1922).—Antiserum for mouse tumor tissue has no retarding effect upon the growth of tumor cells *in vivo* after incubation of the cells with the serum for several hrs. before injection, but exts. of the spleen and lymph glands of the immunized rabbits have some slight retarding effect. Exts. of the spleen and lymph glands from normal rabbits do not possess this inhibiting effect.

H. G. WELLS

**Experimental studies on tumor formation in the internal organs in response to physical and chemical stimulation.** I. Y. KAZAMA. *Gann (Japan. J. Cancer Res.)* 16, 14-8(1922).—Irritation of the stomach, bladder, gall bladder, intestinal canal and uterus was accomplished by mechanical means and by chem. stimulants, lanolin, coal tar, and pityrol being used. "Pityrol" and lanolin produced formation of concretions in the urinary and gall bladder associated with the formation of tumors, occasionally with metastasis. These tumors could not be successfully grafted.

H. G. WELLS

**Relation of antibody to the rate of disappearance of circulating antigen.** G. M. MACKENZIE. *J. Exptl. Med.* 37, 491-509(1923).—In rabbits previously immunized to horse serum the rate of disappearance of horse serum after reinjection is somewhat more rapid than in control animals not previously immunized, but when the av. duration of the persistence of antigen is compared with that in controls, the difference is not impressive. The intravenous injection of large amts. of potent anti-horse rabbit serum immediately after an injection of horse serum does not materially accelerate the rate of disappearance of the horse serum from the circulation. Intravascular union of antigen and antibody is an unimportant factor in the mechanism for the disposal of antigen. By exclusion it therefore appears probable that the rate of disappearance of antigen is largely dependent upon cell avidity for the antigen. Rabbits show a wide range of individual variation in the rapidity with which foreign serum is

appropriated by the tissue cells and in their ability to form precipitins. There does not appear to be any close relation between the amt. of precipitin set free in the circulation and the rate of disappearance of precipitinogen. The type of interrelation between precipitin and precipitinogen in which the precipitinogen diminishes rapidly when the precipitin rises to the crest of its curve is sometimes reproduced in rabbits.

C. J. WEST

KOLLE, WILHELM AND HETSCH, HEINRICH: Die experimentelle Bakteriologie und die Infektionskrankheiten mit besonderer Berücksichtigung der Immunitätslehre. Ein Lehrbuch für Studierende, Ärzte u. Medizinalbeamte. 6th Revised edition. Vienna: Urban & Schwarzenberg. 636 pp.

#### H—PHARMACOLOGY

A. N. RICHARDS

Action of some chemicals on the isolated uterus of mammals. A. CHISTONT. *Arch. Sci. biol.* 3, 53-64(1922); *Physiol. Abstracts* 7, 265.—Small doses of quinine hydrochloride (1:50,000) excite the isolated uterus of mammals; relatively large doses of the same drug (1:5000) have a paralyzing effect. H. G.

Osmotic effects of intravenous injections of sugar solutions. II. M. BÜRGER AND E. HAGEMANN. *Z. ges. expil. Med.* 26, 1-33(1922); *Physiol. Abstracts* 7, 250; cf. C. A. 15, 396.—Expts. *in vitro* showed that the addn. of sugar to an ionic disperse soln. diminishes its power of conduction. This diminution is with the same salt content higher in solns. contg. colloids than in colloid-free solns. Intravenous injections of glucose (1 to 2 g. glucose per kg. body weight) in men cause a hydremic plethora, as measured by the hematocrit method, by refractometric detns., and by detns. of the power of conduction. The hydremia disappears after 1 to 2 hrs., and is not followed by increased diuresis. It is higher in the capillary than in venous blood. The regulation of the osmotic disturbance is damaged in hydropic cases. H. G.

Action of cyanamide. II. E. HASSE. *Z. ges. expil. Med.* 26, 337-51(1922); *Physiol. Abstracts* 7, 264; cf. C. A. 17, 1507.—Cyanamide is a substance which is able to intensify the effect of a series of other substances. Examples are given, also theories. H. G.

Effects of optical isomers of adrenaline bases on glucemia. H. BERRY, F. RATHBERRY AND L. LEVINA. *Compt. rend. soc. biol.* 88, 3-5(1923).—The *l*- and *d*-adrenalinols produce similar changes in the free and combined sugar of the blood plasma but *l*-adrenaline is much more active. The difference in the effectiveness of the two isomers is even more pronounced in the case of the synthetic isoadrenaline (this differs from the normal adrenaline in that the CH<sub>3</sub> is not attached to the NH<sub>2</sub> but to the β-C). *d*-Isoadrenaline is either ineffective or is only very slightly active in doses in which *l*-isoadrenaline is active. S. MORGULIS

Influence of sodium chloride on the elimination of uric acid. P. L. VIOLLE. *Compt. rend. soc. biol.* 88, 62-5(1923).—In a normal individual the presence of an abundance of NaCl within the organism represses the uric acid elimination, while on a Cl-free diet the elimination increases very rapidly. S. MORGULIS

Investigation of the physiological action of sodium ferrocyanide. K. GOLOVANOFF. *Compt. rend. soc. biol.* 88, 161-2(1923).—Cats weighing 2.5 kg. can be given at one time 5-30 g. of Na<sub>2</sub>Fe(CN)<sub>6</sub> without provoking any signs of intoxication. The substance is eliminated through the liver, the kidneys, and the gastric and intestinal mucous membrane. Five g. is eliminated in 3 days; 10 g. in 7 days; 20 g. in 11 days. It tends to accumulate in the liver. The avenues of its excretion explain its diuretic and laxative action. S. MORGULIS

Gastric leucopdesis and oil. M. LORPER AND G. MARCHAL. *Compt. rend. soc.*

*biol.* **88**, 175-6(1923); cf. *C. A.* **17**, 1663.—Leucopidesis into the gastric cavity has been observed following ingestion of oil. The quant. estn. of the migration could not be made, but there seem to be 50-60% polymorphs and 40-50% lymphocytes. The role of the white cells in the digestion was also detd. by *in vitro* expts. A mixt. of sterile olive oil and 1% monobutylin contg. a few drops of phenolphthalein was incubated for 40 min. with one of the following addns.: leucocytes, bile, pancreatic ext.; leucocytes-bile, leucocytes-pancreatic ext., leucocytes-bile ext.; the degree of hydrolysis obtained with each of these additions was measured by the amt. of  $\text{Na}_2\text{CO}_3$  that was required to neutralize the produced acidity. The combination of leucocytes with pancreatic juice gave the most extensive digestion. S. MOROULIS

**Partition of chloroform in the blood.** ARTHUR VAN DESSEL. *Arch. intern. pharmacodynamic* **27**, 1-22(1922).—The venous blood of man under anesthesia was found to contain  $\text{CHCl}_3$  approx. in the same concn. as that of the blood of rabbit, goat and guinea pig and below that of dog blood. The serum takes up more  $\text{CHCl}_3$  than the corpuscles, the distribution being roughly proportional to the lipoidal content of serum and corpuscles. When sep. samples of blood and Ringer soln. are equilibrated in an atm. of  $\text{CHCl}_3$  the former absorbs twice as much  $\text{CHCl}_3$  as the latter. W. A. P.

**The mechanism of alimentary leucocytosis and the role of hydrochloric acid.** P. PAGNIEZ AND A. PLICHET. *Presse med.* **31**, 77-8(1923).—The ingestion of 50-150 cc. of 0.4%  $\text{HCl}$  caused in normal subjects an increase of the no. of white cells, especially of the polymuclear cells, in the blood, this increase being quite analogous in degree and in duration to that observed after the ingestion of a protein-rich meal. A patient suffering from a gastric neoplasm and showing a marked achlorhydria, and who usually reacted with a fall in the no. of leucocytes after a protein meal (milk), showed a distinct leucocytosis after the ingestion of  $\text{HCl}$ . This leads the authors to believe that the secretion and absorption of  $\text{HCl}$  during digestion furnishes at least one factor in the mechanism of alimentary leucocytosis. W. A. PERLZWEIG

**Comparative studies on respiration. XXIV: The effects of chloroform on the respiration of dead and of living tissue.** G. B. RAY. *J. Gen. Physiol.* **5**, 469-77(1923).— $\text{CHCl}_3$  at a concn. of 0.25% (in van't Hoff's soln.) caused an increase in  $\text{CO}_2$  production followed by a decrease in the marine alga, *Ulva lactuca* var. *latissima*. 0.5% caused a decrease which started at once. Placed in 1%  $\text{H}_2\text{O}_2$  in van't Hoff's soln., the rate of  $\text{CO}_2$  output was diminished; on the addn. of 0.0005  $M$   $\text{Fe}_2(\text{SO}_4)_3$  the rate was increased. The same concn. of  $\text{Fe}_2(\text{SO}_4)_3$  without  $\text{H}_2\text{O}_2$  caused 1st. an increase followed by a decrease in the rate. When *Ulva* is killed in such a way that the oxidizing enzymes are destroyed,  $\text{CO}_2$  is not produced unless  $\text{H}_2\text{O}_2$  and  $\text{Fe}_2(\text{SO}_4)_3$  are present. If  $\text{CHCl}_3$  is added to this mixt., an increase in  $\text{CO}_2$  production followed by a decrease results when the concn. of  $\text{Fe}$  is low. When the  $\text{Fe}$  concn. is high, the rate seems to decrease from the start. CHAS. H. RICHARDSON

**The influence of benzene upon certain aspects of metabolism.** F. P. UNDERHILL, AND B. R. HARRIS. *J. Ind. Hyg.* **4**, 491-500(1923).— $\text{C}_6\text{H}_6$  "acts not only on the blood elements but exerts a catabolic influence on body tissues as a whole, as manifested by a sharp rise in creatinine and total N, within a very short period after its subcutaneous injections into rabbits, far in excess of that found in rabbits under similar conditions under ordinary starvation." GEORGE ERIC SIMPSON

**Urinary antiseptics: A study of the antiseptic properties and the renal excretion of 204 aniline dyes.** E. G. DAVIS. *Am. J. Med. Sci.* **161**, 251-67(1921).—Of 204 aniline dyes tested 61 had antiseptic properties in an agar medium, and 28 were efficient as antiseptics when added to urine. Many of the dyes (44) showed selective bactericidal action, the Gram-negative *B. coli* being always more resistant than staphylococci. The effect of the dyes was greater in alk. urine than in acid. Only 3 of 37 azo dyes

showed antiseptic action, and this was weak. Many of the triphenylmethanes were antiseptic, but they were also toxic. Of 21 dyes of the xanthine group 3 were antiseptic, and 2 were excreted in the urine. Two of 4 acridine dyes were antiseptic. Of 9 dyes of the azine group 5 were active and of these 3 were excreted and were non-toxic. Only two of the dyes (proflavine and acriflavine) gave an antiseptic urine when the dye was administered intravenously.

G. H. SMITH

**Blood changes after administration of urea.** NONNENBRUCH. *Arch. expl. Path. Pharmacol.* 89, 200-18(1921).—Urea in large amts. was administered to man and rabbits by mouth and by intravenous injection, and the amts. of urea in blood and tissues were detd. A normal residual N does not mean a lack in N retention, and conversely, a high value for residual N does not imply N retention. The course of the residual N curve and the rapidity of N excretion in the urine are related chiefly to the amt. of fluid given. In diabetes the residual N fell after urea administration; after artificial polydipsia the normal level returned within 10 hrs. after the administration of 40 g. Intravenously injected urea quickly disappears from the blood, but before elimination by the kidney the urea is returned from the tissues to the blood. In the distribution of urea in the tissues, active factors other than perfusion are operative. Detns. of the erythrocyte count, NaCl or protein content of the blood indicate that these factors bear no fixed relation to the processes involved in excretion of urea.

G. H. SMITH

**Theory of the retention and excretion of absorbed bromine salts and the halogen content of the organism.** FR. BAUR AND E. OPPENHEIMER. *Arch. expl. Path. Pharmacol.* 94, 1-21(1922).—A mathematical treatment, with the derivation of a formula expressing the relation between Br administration and Cl elimination. The excretion of NaCl bears a direct relation to the amt. of NaBr ingested. The relations between Cl and Br in the organism are such that the so-called Br equil. is never obtained, since an organism which has once received Br never becomes Br-free.

G. H. SMITH

**Mechanism of the contraction of striated muscle induced by poisons.** V. Action of specific muscle poisons on non-living colloids. OTTO RIESSER AND S. M. NEUSCHLOSZ. *Arch. expl. Path. Pharmacol.* 94, 190-221(1922); cf. *C. A.* 17, 1082.—The effects of veratrine, strophanthine, digitalis, quinine, caffeine, nicotine, and novocaine upon striated muscle and upon gelatin solns. were compared. In general, those poisons which modify the viscosity of gelatin solns. in the same manner, react upon muscle with the same biological effects; those of diff. biol. effect react differently with gelatin soln. Poisons which have a marked physiol. action, but which do not attack the contractile substance of muscle, fail to change the viscosity of gelatin solns. The mode of action upon muscle is reproduced in gelatin solns. insofar as the antagonism between veratrine and novocaine (and atropine) is concerned.

G. H. SMITH

**Action of digitalis, calcium, and barium upon heart muscle strips, and the antagonistic effects of cocaine, magnesium and potassium.** MARTIN BRANN. *Arch. expl. Path. Pharmacol.* 94, 222-34(1922).—Contrary to the assertion of Löwe, digitalis applied to a strip of ventricular muscle which contains no auricular elements induces a contraction which is abolished by both cocaine and  $\text{CaCl}_2$ . Since such heart muscle prepns. contain no ganglion cells the effect of digitalis cannot be upon such cells, but is rather upon the musculature peripheral to the nerve-ending but central to the muscle substance proper. Digitalis and  $\text{CaCl}_2$  must attack the same place, and indeed the contraction due to this salt is abolished by cocaine,  $\text{MgCl}_2$  and  $\text{HCl}$ . Ba acts somewhat distinctively, since its tonic effect is uninfluenced by cocaine, although it is abolished by Mg and K. Thus, digitalis, cocaine, and Ca attack the same elements, and Ba, Mg, and K react upon the muscle through the same general region.

G. H. SMITH

**Elimination through the salivary glands and the gastric mucous membrane of alkaloids subcutaneously administered.** K. J. HUBER. *Arch. expl. Path. Pharmacol.*

94, 327-51(1922).—Morphine was excreted by dogs and rabbits through the stomach and the urine. Cocaine was eliminated by the stomach in cats, by the urine in rabbits. Caffeine was excreted through both stomach and kidneys; theobromine by the kidneys. Quinidine appeared in the urine; curarine in the stomach and urine. Quinine was found in the stomach, intestine and urine. In dogs, strychnine appeared in the stomach, the saliva, the urine and the sweat. Brucine and antipyrine were found in the stomach. Very little atropine is excreted in the urine in cats, although in rabbits 15%, and in dogs 33.4% of the amt. injected is eliminated through the kidneys. In frogs the detoxicating organ is the liver. In rabbits most of the atropine is destroyed in the blood. In dogs, even after large doses, atropine and physostigmine did not appear in either stomach or saliva. Arecoline was found in the saliva, not in the stomach. Papaverine and veratrine were excreted through the stomach. In reacting to alkaloids destructive or detoxicating forces are of primary importance, avenues of elimination are secondary. Of the latter the kidney and intestine are more significant than the stomach and salivary glands.

G. H. SMITH

Biological Röntgen-ray action. I. Increasing and limiting biologic ray action. PH. ELLINGER AND OSCAR GANS. *Arch. expil. Path. Pharmacol.* 95, 291-303(1922).—Sensitization with 10% Th(NO<sub>3</sub>)<sub>4</sub> not only increases the action of Röntgen rays in their biol. action but facilitates penetration.

G. H. SMITH

Ionic theory of stimulation. V. Restoration of susceptibility in nerves after stimulation. P. P. LAZAREV. *Arch. ges. Physiol. (Pflüger's)* 197, 468-70(1923); cf. C. A. 16, 2877.—Mathematical, with a statement of the laws governing the restoration of susceptibility in nerves after stimulation. Exptl. data agree with the chem. theory.

G. H. SMITH

Electronarcosis. K. v. NEERGAARD. *Arch. klin. Chir.* 122, 100-50(1922).—The possible usefulness of electronarcosis was detd. by animal expts. All factors, essential to make the method of broad practical application, are not yet known. As compared with inhalation narcosis the elec. method has many points in its favor.

G. H. SMITH

Blood sugar changes associated with operations under local and ether anesthesia. HANS DEWES. *Arch. klin. Chir.* 122, 173-87(1922).—In extraperitoneal operations the local application of novocaine-suprarenine solns. for narcosis leads to a slight increase in blood sugar; the increase corresponds to that following the injection of the soln. without operation. In laparotomies the increase in blood sugar is greater, either with local or ether narcosis. The rise in sugar may amt. to 2.5 to 4 times the normal value. Postoperative glucosuria may follow anesthesia of either type, with or without a corresponding change in blood sugar.

G. H. SMITH

Note on the toxicity of castor oil seed. EDWIN DOWZARO. *J. Am. Pharm. Assoc.* 12, 116-7(1923).—The smallest dose of *Ricinus communis* per os which proved fatal to guinea pigs is 0.179 g. per kg. of animal of seeds with dark skin removed. If the proportionate toxicity holds true for man, 12.29 g. would be required to kill a man of 150 lbs. wt.

L. E. WARREN

Chemical and pharmacological relations of unsaturated radicals (BRAUN, SCHIRMACHER) 10.

WALLON, EMILE: Le bismuth dans le traitement de la syphilis. Paris: Les Presses Universitaires de France. 96 pp. Fr. 5.

## I—ZOOLOGY

R. A. GORTNER

Morphological investigations on the silk secretions in the silk worm. M. YAMANOUCHI. *J. Coll. Agr. Hokkaido Univ.* 10, Pt. 4, 1-49(1922).—A histological study of

the silk secretion mechanism of the silk worm, showing that fibroin has its origin in the posterior parts of the gland while sericin originates in the middle parts. Fibroin and the silk gelatin, sericin, are always present sepd. from each other. F. A. C.

The influence of reaction on fresh-water infusoria. W. G. SAVICH. *Bull. Inst. Exptl. Biol.* (Moscow) 1, 36-48(1921); *Physiol. Abstracts* 7, 165. —S. studied the longevity of these in solns. of varying H-ion concn. For several kinds this optimum was an acid medium ( $p_H = 6.23-6.97$ ), for others—in an alk. medium ( $p_H = 7.16-9.18$ ). To the former belong *Frontonia*, *Bursaria*, etc.; to the second belong *Nassula*, *Paramacium*, *Stentor*, etc. Several kinds (*Dileptus*) can live well within wide limits ( $p_H = 4.49-9.18$ ). S. notes the favorable influence of small admixts. of Ca. The osmotic pressure does not play a great part in the well-being of infusorians. H. G.

Dextrose in eggs of vertebrates. G. GORI. *Atti accad. fisiocrit. Siena* 21, 711-6 (1920).—Dextrose is absent from the yolks of eggs of *Torpedo* and of fishes; the amt. of urea present is insufficient to obscure the reaction. With material dried first at  $45^\circ$  and then in a vacuum, dextrose was found to be absent from mammalian ova, present, combined and free, in birds' eggs, and present in the free state in amphibian eggs. J. C. S.

The reciprocal relationship between organic phosphorus combinations and the inorganic phosphates in the animal organism. YASURA MASAI AND TOKUJIRO FUKUTOMI. *J. Biochem.* (Japan) 2, 271-7(1923).—In the course of development of the hen egg the phosphatide P diminishes slowly at first, then abruptly up to the 14th day of incubation. The protein P also diminishes rapidly after the 18th day of incubation. This P which becomes split off from its organic combination is obtained in acid soln. together with the phosphates. From the 16th incubation day the phosphate P increases very rapidly. The vitellin P which constitutes the greatest portion of the protein P diminishes gradually up to the 16th day and rapidly disappears entirely. The loss in the vitellin P seems to coincide with the increase in nuclein P. S. MORGULIS

Respiration of fish and the reaction of the water. FRANCE GUEYLARD AND MARCEL DUVAL. *Compt. rend. soc. biol.* 88, 180-2(1923).—No matter what the initial  $p_H$  value of the water neutrality is reestablished either through the  $CO_2$  or through  $Na_2CO_3$  given off by fish. S. MORGULIS

The action of an electrolytic colloid, Congo red, on sea-urchin eggs. R. COURRIER. *Compt. rend. soc. biol.* 88, 196-7(1923).—Placed in a soln. of Congo red dissolved in sea water, sea-urchin eggs do not become colored and segment normally. Unfertilized eggs, however, become permeated by the coloring matter. This produces the following effects: failure of formation of the fertilization membrane, penetration by a number of sperms and lack of segmentation. S. MORGULIS

Oxyhemoglobin present in back swimmer, *Buenoa margaritacea*. H. B. HUNGERFORD. *Can. Entomol.* 54, 262-3(1923).—Hemoglobin was found in cells grouped about the tracheal trunks connected with the abdominal spiracles; it first appears in the embryo. It gave the characteristic spectroscopic and guaiac tests; also the hemin crystals. Hemoglobin has previously been found among insects in the blood worm (*Chironomus*) where it is free in the body cavity and in *Gastrophilus equi*, where it is found in certain cells related to the tracheal system. This records its first occurrence in the Hemiptera. The histology and development of the hemoglobin-contg. cells are being studied. CHAS. H. RICHARDSON

Hydrogen-ion concentration of sea water in its biological relations. W. R. G. ATKINS. *J. Marine Biol. Assoc.* 12, 717-71(1922).—A general description of H-ion concn., its meaning and the various methods of its detn. in sea water, is given. The literature is reviewed up to 1921 and the following topics are proposed for study: (1) The  $p_H$  concn. of the water of the aquarium tanks as compared with that of Plymouth

(England) Sound and the town fresh water supply. (2) The relation of Sound water to that of tide pools, and (3) to that of Sound water over sea weeds in shallow parts. (4) The variation of Sound water with the tide and time of day. (5) The relation of  $p_H$  salinity and temp. of the Sound water to the corresponding values in the open sea. (6) Factors affecting  $p_H$  of the open sea, such as sunlight, photosynthesis, respiration, aeration, temp. and salinity. (7) Correlation of the  $p_H$  and seasonal variations in the marine fauna and flora. The colorimetric details of  $p_H$  were made according to the method of Clark and Luhs. *Conclusions:* (1) The salt error of cresol red for sea water of salinity 35 per 1000 is  $p_H$  0.18 when detd. with Clark and Luhs' standard borate buffer mixts. and compared with McClendon's set as corrected by potentiometer measurements. The measurements are believed to be accurate to  $p_H \pm 0.01$ . To attain this accuracy the indicator must be measured with exactness, not by drops. (2) Sea water may become as alk. as  $p_H$  9.7 as a result of very active photosynthesis. This it does in virtue of the presence of Mg salts since the limiting  $p_H$  value of  $MgCO_3$  is 10.0, the same as for  $Mg(OH)_2$ .  $CaCO_3$  as pure calcite gives a  $p_H$  limiting value of 9.0. (3) The saltwater tanks of the aquarium are always less alk. than the water of Plymouth Sound, or as 7.6 to 8.1. Any lowering of the  $p_H$  for the tanks below 7.6 denotes an abnormal excess of  $CO_2$ ; at 7.3 symptoms of distress may appear among the fishes; and at 7.1 the water is foul and bad smelling. Water around rotting sea weed in a jar may be as acid as 6.4. Agitation of water from the tanks with air results in the removal of  $CO_2$  and a  $p_H$  value of 8.0 is attained. (4) A slight drop in  $p_H$  of 0.05 may be observed between high and low water. Over *Laminaria* in shallow water,  $p_H$  may be 0.15 more alk. than the general mass of water. Rock pools in summer may be 0.25 more alk. and  $2.5^\circ$  warmer. (5) During July the water of the Sound was about 0.12 more alk. than that of the open sea but becomes less alk. in Aug., a min. being reached in Dec. (6) In the open sea between July and Dec. the  $p_H$  value varies from 8.27 to 8.14. The April figure was 8.24. A storm, by mixing  $CO_2$  with the water, may reverse the normal gradient. (7) From the change in titration value it is estd. that the min. amt. of carbohydrate photosynthesized as dextrose is 1 kg. per 4 sq. m. of surface between July and Dec. (8) The ranges of  $p_H$ , salinity and temp. under which marine plants and animals exist are tabulated for aquarium tank, shallow water, rock pool, Plymouth Sound, Plymouth Breakwater, and 20 miles out to sea. Respirable organic matter of sea water. *Ibid* 772-80.—(1) On storing, sea water suffers a decrease in  $p_H$  value, the amt. of change being equiv. to 1.0 to 3.0 cc. 0.01 *N* acid to 100 cc. of sea water. This decrease of  $p_H$  is caused by the production of  $CO_2$  by organisms. (2) The change corresponding to 1 cc. of acid, as above, is equiv. to that produced by the complete oxidation of 3 mg. per l. of hexose sugar, which requires 3.2 mg. per l. of O. This does not agree with the usual results for O consumed by the alk. permanganate method. The difference is attributed to respiratory changes taking place in the water during storage which set free much of the organically combined C before oxidation by permanganate has been started. Detns. on freshly drawn filtered sea water give, according to Ruben, 7.5 mg. of hexose or 8.0 mg. of O consumed. (3) It is probable that the change in  $p_H$  value on storing indicates the amt. of plankton present, assuming the absence of sewage. (4) The total amt. of C elcd. as hexose, which is set free during storage by respiration in sea water 20 miles out from Plymouth, is about twice that photosynthesized between July and Dec. Dihromothymolsulfonephthalein as a reagent for determining the hydrogen-ion concentration of living cells. *Ibid* 781-3.—Bromothymol blue may be used in dil. soln. for ascertaining the  $p_H$  of certain marine organisms. It penetrates slowly, but the stained portions remain actively motile, so its toxic action does not appear marked with the dils. used. *Pleurobrachia pileus*, *Clytia Johnstoni*, and *Tiara pileata*

gave  $pH$  values from 6.2 to 7.5, though the more alk. end of the range may be pathological. About 0.2 should be subtracted from these figures for neutral salt error. The sea water used was initially at  $pH$  8.2, corr. Hydrogen-ion concentration of the cells of some marine algae. *Ibid* 785-8.—Care was taken to wash the thallus rapidly in fresh [sea?] water before crushing, or to wash and excise portions of the interior with a stainless knife. The specimens were taken from Plymouth Beach from sea water with  $pH$  about 8.2, toward the end of April. *Laminaria digitata*, *L. saccharina* and a species of the genus *Nilophyllum* gave  $pH$  of 7.3; *Fucus platycarpus* and *Ceramium rubrum* 7.2; *Himanthalia lorea*, liquid from disk 6.9, from strap 6.6; *Ulva latissima* 7.0. These results show that the sap of these marine algae is in most cases neutral and in no case of the pronounced acid character of the sap of many land plants. It follows that the enzymes concerned in the metabolism of these algae must be quite different from those which effect corresponding changes in land plants. Influence upon algal cells of an alteration in the hydrogen-ion concentration of sea water. *Ibid* 789-91.—Sea water originally at  $pH$  8.2 became as alk. as 9.4 by the photosynthetic action of *Ulva latissima* L. in removing  $CO_2$ . This degree of alk., did not prove injurious to *Ulva*, but exposure to it for 2.5 hrs. at  $27^\circ$  sufficed to increase the permeability of the superficial cells of *Ceramium rubrum* irreversibly and fatally. Similar though less rapid changes brought about the death of numerous *Vorticellae*, epiphytic on *Ceramium*. The criteria for living cells were permeability to neutral red and impermeability to bromocresol purple. These facts may have a bearing upon the distribution of these and similar algae upon the shore. Preparation of permanently non-acid formalin for preserving calcareous specimens. *Ibid* 792-4.—Formalin which is permanently non-acid and only slightly alk., close to  $pH$  9.0, may be prepd. by the addition of borax to the dild. formalin until a bright red is shown with phenolphthalein, or a slaty blue with thymol blue. Distn. of formalin from solid  $MgCO_3$  gives an acid product,  $pH$  4.4. Formalin neutralized with  $NaOH$  becomes acid on standing, the change being hastened by light. Com. formalin may be as acid as  $pH$  2.8. L. W. R.

## 12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

The protection of vitamin C in foods. E. F. KOHMAN. *Ind. Eng. Chem.* 15, 273-5 (1923).—In studies of the stability of vitamin C toward heat, insufficient account has been taken of the role of O in its destruction. O is removed more effectively from a liquid exposed to diminished pressure if the container is shaken or jarred. To remove the O from solid foods without heat, subject to high vacuum, under water or without water, and release the vacuum with N. Respiration of fruits and vegetables may be utilized to diminish their O content.

C. J. V. PETTIBONE

The water buffalo for dairy purposes. C. O. LEVINE. *Lingnaam Agr. Rev.* 1, 1-30 (1922); cf. *C. A.* 13, 1231; 14, 1392, 2385.—The history, present distribution, description and uses are given. Tables give the analysis of the milk and the production records of cows for entire lactation periods. The av. % fat of the milk from 23 cows for 25 lactation periods was 11.05. Analyses are given of 10 samples of milk. The av. % fat was 12.46, ash 0.89, protein 6.03, sugar 3.74 and total solids 23.29. Usually there is a steady increase in % fat from the beginning to the end of the lactation period. The milk and the butter are pure white and are wholesome and palatable.

O. L. EVENSON

Fats in the evaporated-milk industry. H. F. ZOLLER. *Ind. Eng. Chem.* 15, 278-9 (1923).—Comparison of the physical properties and certain chem. values of butter fat and coconut oil show that the latter is more suitable than any other natural industrial



fat for compounding with skim milk in the production of a sterilized canned product. Cottonseed oil if hydrogenated to the proper point reduces the iodine number near to that of coconut oil; by proper treatment in the vacuum pan the hydrogenation flavor is removed and it then can be used to compound with skim milk to the same end.

H. F. Z.

**Sodium chloride content of milk.** C. PORCHER. *Lait* 3, 11-21(1923).—NaCl varies widely. A relation seems to exist between the lactose and NaCl content of milk as affecting the osmotic pressure and consequent cryoscopic point. A milk with a high lactose content usually shows a low NaCl content; the converse is equally true. Thus these crystalloids serve to establish the constancy of the cryoscopic value. H. F. Z.

**Milk analysis by semi-microchemical methods.** H. LÜHRIG. *Milchwirtschaft. Zentr.* 51, 157-9, 169-72(1922).—To save reagents use small amts. of material. Two cc. of milk are used for sp. gr. instead of the usual 25 or 50 cc. The % fat is detd. by the Rose-Gottlieb method on 1 cc. of milk, the amts. of the other reagents being diminished accordingly. 1 g. or less is used for total solids, acidity, lactose, N and sp. gr. and ash of the serum. Time is saved and in the acidity detn. the end reaction is sharper. A few results obtained by these methods are given. O. L. EVENSON

**Influence of mustard extract on the coagulation action of rennin.** F. DRUGG. *Lait* 2, 808-9(1922).—Mustard ext. has no appreciable retarding action on rennin coagulation of cow milk. H. F. ZOLLER

**The chemist enters a new industry.** H. C. BARNARD. *Ind. Eng. Chem.* 15, 449-50(1923).—An address about the chemist in the baking industry. E. J. C.

**Chemical composition of millet flour.** G. QUAGLIARIELLO. *Atti com. sci. aliment. accad. Lincei* 1921, reprint 20 pp.; *Physiol. Abstracts* 7, 183.—Millet flour contains a good deal of fat and cellulose and a relatively small amt. of proteins; it cannot be recommended for human consumption. H. G.

**The precipitation of proteins from cereal extracts by sodium tungstate.** L. A. RUMSEY. *Ind. Eng. Chem.* 15, 270-72(1923).—The Na tungstate reagent of Folin and Wu is applied to the pptn. of proteins from wheat flour exts. Neutral 5% suspensions or exts. of flour are freed from proteins by 15%  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  soln. followed by dropwise acidification with concd.  $\text{H}_2\text{SO}_4$  to pH of 2 or less. Thymol Blue serves as an indicator. Centrifuging produces a clear soln. for detn. of reducing sugars directly by the Munson-Walker method. All filtrations are eliminated. Diastatic action is completely inhibited by tungstate clarification, but not by lead acetate. Five min. is sufficient for clarification. I. A. R.

**Action of shortening in the light of the newer theories of surface phenomena.** WASHINGTON PLATT AND R. S. FLEMING. *Ind. Eng. Chem.* 15, 390-4(1923).—The physical effect of shortening on the structure and physical properties of the dough and finished sugar cookies was studied. In this type of product shortening acts by interposing itself in layers between the particles of dough, thereby preventing the formation of one continuous mass. This structure can be observed with the microscope in both the dough and baked product. Plasticity of different fats at the temp. of mixing (about 80° F.) is an important factor in causing differences between their shortening power. The shortening power for plastic fats is detd. by the plasticity and unsatd. glyceride content and by the latter for fats not plastic in the dough. This is in accord with the present ideas regarding orientation of mols. and the energy relations at interfaces. The parallelism between shortening and lubrication is pointed out. H. A. LEPPEP

**Processing canned corn.** W. D. BIGELOW. *Canning Age* 1923, Feb. no., 25, 56.—Minimum times and temps. for destroying resistant strains of *B. botulinus* in the canning of corn are given. H. A. LEPPEP

**Processing string beans.** W. D. BIGELOW. *Canning Age* 1923, Feb. no., 58.—

Min. times and temps. for destroying resistant strains of *B. botulinus* in the canning of string beans are given.

H. A. LEPPER

**Effect of hard water on peas.** A. R. STEVENSON. *Canning Age* 1923, Feb. no., 21-2.—The effect of hard water on peas in various steps in the canning process is discussed. Many grades of NaCl used have a Ca and Mg content sufficient to have a distinctly hardening effect on peas. NaCl with Ca content of more than 0.25% as CaCO<sub>3</sub> should not be used.

H. A. LEPPER

**A short cut to a technical analysis.** L. V. STRASBURGH. *Canning Age* 1923, Feb. no., 62, 64.—A quick and easy method is given for *detg. sp. gr. of tomato pulp* based on the balance of the pulp against a test soln. consisting of CCl<sub>4</sub> and Varnolene (Standard Oil Co. petroleum product). The method can be used in factory control and in the trade.

H. A. LEPPER

**Experiments in apple packing.** B. S. CLARK. *Canning Age* 1923, Feb. no., 17-9, 68, 70.—The gas in 11 varieties of Michigan apples was shown by analysis not to be air but undoubtedly the result of natural respiration. Results of gas liberation by soaking in NaCl soln. are given with an application of the findings to problems of canning apples.

H. A. LEPPER

**Chemistry of the pecan.** W. G. FRIEDMANN. *Proc. Okla. Acad. Sci., Univ. Okla. Bull.* 1922, N. S., No. 247, 71.—The pecan contains 40 to 60% kernel. An av. of 14 analyses of the pecan kernel gave H<sub>2</sub>O 3.2%, ash 1.57, protein 11.0, crude fiber 2.2, N-free ext. 10.04, fat 71.99. The carbohydrates are sucrose 9.03%, invert sugars 21.90, araban 14.82, methylpentosans 1.68, cellulose (crude fiber) 14.29, amyloid 4.54, tannins 2.37, other hemicelluloses etc., 31.17. The protein was found by Cajori, also by Dowell and Menual, to be a globulin. The N distribution was amide N 9.8%, humin 3.6, arginine 23.0, histidine 3.7, cystine 0.8, lysine 5.9, monoamino 62.0, non-amino 0.8. Pecan oil according to Deiller and Fraps had a sp. gr. at 15° of 0.9184, sapon. value 189.0, iodine value 106.0, Reichert-Meissl value 2.2, insol. fatty acids and unsaponifiable matter 93.4.

I. W. RIGGS

**Fruit jellies. I. The role of acids.** L. W. TARR. Delaware Agr. Exp. Sta., *Bull.* 134 (*Tech. Bull.* 2) 37 pp.(1923).—The acidity factor in fruit jellies was studied, the pectin, sugar, and water factors being maintained as nearly const. as possible. The formation of fruit jellies cannot be correlated with total acidity and there is a direct relation between jelly formation and active acidity or H-ion concn. The min. H-ion concn. at which jelly formation occurs is  $p_H$  3.46 for the purest source of pectin. The concn. of H ions controls the formation of the jelly; the anions exert no effect that could be observed. Jelly formation occurs irrespective of the quantity of pectin present, once the min. H-ion concn. is attained. The quantity of pectin, however, must equal the min. amt. that is necessary to produce jelly. The presence of neutral salts probably reduces slightly the min. H-ion concn. at which the jelly can form. With pectin, sugar, and water const., the character of the jelly is also detd. by the H-ion concn. The jelly becomes stiffer as the H-ion concn. increases. Syneresis occurs when the H-ion concn. is much greater than  $p_H$  3.1. There is a stoichiometrical relation between pectin and the combining power of the acids. Tartaric acid is probably the most efficient of the acids commonly in the fruit juices that are used for jelly making. Citric acid is probably the least efficient. Malic acid lies probably between these two. The H-ion concn. of ordinary fruit juices depends upon the particular acids present, and upon the "buffer" action exerted by the particular juice.

J. J. SKINNER

**The composition of dawa-dawa pods from the Gold Coast.** ANON. *Bull. Imp. Inst.* 20, 461-3(1922).—Dawa-dawa (*Parkia* sp., probably *P. filicoidea*, Welw.) pods consist of pod-case 41.2, soft yellow powdery material 33.4, and seeds 25.4%. An aq. ext. of the pod-cases contained tannin and also material of a pectic nature having

adhesive properties. Analysis of (1) powdery material, (2) seeds, (3) powdery material and seeds (calcd. to the relative proportions in which they occur in the pods), and (4) powdery material and seeds of *P. filicoidea* from Nigeria gave, resp., moisture 13.7, 10.1, 12.14, 9.35; crude proteins 4.2, 28.5, 14.70, 16.0; fat 2.0, 16.8, 8.39, 6.14; reducing sugars (as dextrose) 19.2, nil, 10.90, 20.87; non-reducing sugars (as sucrose) 8.5, 3.5, 6.34, 1.35; other carbohydrates (by diff.) 35.8, 28.9, 32.83, 30.33; crude fiber 12.6, 8.3, 10.74, 11.0; ash 4.0, 3.9, 3.96, 4.78; nutrient ratio 1:16.2, 1:2.5, 1:4.7, 1:4.2; food units 79, 146, 108, 108. Neither the powdery material nor the seeds contained alkaloids or cyanogenetic glucosides. They are both of satisfactory compn. as foodstuffs. The % of fat in the seeds is probably not large enough to render them of com. value as a source of fat.

A. P.-C.

**Nutritional value of the grain sorghums.** PAUL MENAUL. *Proc. Okla. Acad. Sci., Univ. Okla. Bull.* 1922, N. S., No. 247, 16-8.—Three groups of animals were fed exclusively yellow milo, darso and white kafir, resp., and a 4th group was used as controls. At the end of 1 month of such feeding growth ceased in each group. Protein from milk was purified from the so-called vitamins and added to the diet so that the ration consisted of sorghum 90%, milk 7 and salt 3. The control animals received in addition to this ration fresh milk and vegetables. Growth was resumed and after 2 months of this feeding the growth of the first 3 groups was about the same as that of the control group. The 3 types of grain sorghum tested appear about equal in nutritional value. Darso is distasteful to some animals. The nutritional failure of grain sorghums, when fed exclusively, is due to the nutritional incompleteness of their protein fraction.

I. W. RIGGS

**Report of the Swiss fruit, wine and horticulture experiment station in Wädenswil for 1917-20.** *Landw. Jahrb. Schweiz.* 36, 765-968(1922).—The report is divided into: (1) Plant physiology and plant pathology, (2) fermentation and bacteriol., (3) chem. and (4) technical sections. The chem. section deals with the analysis and investigation of wines and fruit juices.

O. J. EVENSON

The active principles of some South African plants (JURITZ) 11D. Utilization of lime seeds (ANON.) 27. Apparatus for spray desiccation of milk or other liquids (U. S. pat. 1,450,840) 1. Air control for drying apparatus (for milk) (U. S. pat. 1,449,115) 1.

**Actual Methods of Analysts Employed in the Municipal Laboratory of Paris and Papers on Matters Relating to Nutrition. I. Animal Products and Preserved Foods.** Edited by A. Kling. Paris: Dunod. 326 pp. Reviewed in *Exptl. Sta. Record* 47, 715(1922).

**Bread containing cereal germs.** D. CHIDLAW. U. S. 1,450,483, Apr. 3. Germs of wheat or other cereals are added to bread dough after about 70% of its period of fermentation has elapsed, so that the undesirable action of the enzymic or other substances associated with the germs will not take place during the entire period of dough conditioning.

**Powdered "modified milk substitute."** A. W. BOSWORTH. U. S. 1,450,836, Apr. 3. A dry prepn. which forms a relatively stable emulsion with H<sub>2</sub>O and is adapted for feeding infants is formed from edible fats, lactose, sol. casein, whey powder and citric acid proportioned so that on addn. of H<sub>2</sub>O the compn. gives an analysis similar to that of human milk.

**Sweetened condensed milk.** T. MOJONNIER. U. S. 1,449,688, Mar. 27. Fresh milk is condensed with sugar in a vacuum pan and the condensed product is cooled in

one unit and crystn. is effected in one of another series of units the remainder of which are at the same time filled without exposure to air and in continuous operation.

"Meat-like" preparation from keratin. B. REWALD. U. S. 1,448,281, Mar. 13. C. of high gas-absorbing power is added to keratin and the mixt. is boiled with an inorg. acid until amino acids are formed. The soln. is then neutralized.

### 13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

Some forces of the earth which await development in connection with the chemical industry. BERTHOLD BLOCK. *Chem. App.* 10, 27-30(1923).—A general discussion of the desirability of a better utilization of the energy in peat, coal, steam, tides, winds, atm. electricity, and the heat from volcanoes, hot springs and the sun. J. H. M.

The progress of the British chemical industry since 1914. H. LEVINSTEIN. *Chemistry and Industry* 42, 250-62, 294-7(1923). E. H.

Evaluation of transformer oils. HANS STRÄGER. *Helvetica Chim. Acta* 6, 62-86 (1923).—Besides the required physical and elec. properties, suitable transformer oils must undergo only slight decompn. at high temp. in the presence of O and certain metals, and the products of the decompn. must have the smallest possible action upon the insulating materials, *e. g.*, cotton, with which they come in contact. Comparative tests were made upon 6 samples of commercial transformer oils, by the methods commonly employed for detg. durability. The sludge formed is of two types: sol. in oil, and insol. in oil. Asphaltogenic acids constitute only a small part of the sludge, the chief part being a mixt. of highly polymerized O compds., similar to asphalt. By the catalytic action of Cu, oil-sol. acids and unsatd. cyclic compds. are formed in the presence of air. No direct relationship between sludge formation and chemical consts. such as I no., formolite no., etc., could be discovered. Cotton is attacked by the products of oxidation, products similar to oxycellulose being formed. At higher temps. carbonization of cellulose takes place, the oil acting as a source of active O. It is not sufficient to compare oils by detg. a single product of the reactions, such as the acids formed. The following test is proposed. About 1200 cc. of oil is heated for 1000 hours at 112°, the temp. being controlled automatically. After stirring thoroughly, small samples are removed at the end of 100, 200, 300, 500 and 1000 hrs. The samples are mixed with twice their vol. of benzine (h. 50°), and allowed to stand for 24 hrs. The ppt. formed is collected on a filter, washed with benzine, dissolved in a Soxhlet app. with  $\text{CHCl}_3$ , and weighed after evapn. of the  $\text{CHCl}_3$ . After dissolving in  $\text{C}_6\text{H}_6$ , the asphaltogenic acids are detd. by saponifying with alc. KOH, removing the alc. soln. of the salts of the acids, liberating the acids with HCl, dissolving in  $\text{C}_6\text{H}_6$ , and weighing after evapn. of the  $\text{C}_6\text{H}_6$ . The sludge insol. in oil was detd. by filtering the oil while hot (80°), washing the filter with benzine, adding the washings, after distn. of the benzine, to the filtrate, and weighing. W. F. FARAGHER

Lubricating oils containing soap. HANS VON DER HEYDEN. *Chem.-Zig.* 47, 170 (1923).— $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  are used as the basis for soaps in oils and can be detd. by the ash content. They increase the viscosity and thus imitate genuine oils but should not be used in combustion motors. E. SCHERUBEL

Investigations on oil. J. E. HRESTERMAN. *Z. Hyg. Infektionskrankh.* 96, 161-9 (1922).—Machine and other mineral and vegetable oils the handling of which has led to toxic symptoms among workers were studied to locate the toxic principal. It was not found to be associated with the degree of unsatn. of the free acids, with substances basic in character or with the asphalt materials. It seemed to belong to the more volatile constituents of the oil and is removed or destroyed by  $\text{H}_2\text{SO}_4$ . F. A. C.

Hydrometer [for lubricants] (U. S. pat. 1,449,334) 1.

ANDRÉ, LOUIS EDGAR: *Vegetabilische und Mineralmaschinenöle* (Schmiermittel). 2nd Ed. Vienna & Leipzig: A. Hartleben. 504 pp.

BAUD, PAUL: *Chimie industrielle. La grande industrie chimique. Les métalloïdes et leurs composés. Les métaux et leurs sels. Industries organiques*. Paris: Masson et Cie. 704 pp. Fr. 40.

MARTIN, GROFFREY: *Industrial and Manufacturing Chemistry. A practical Treatise. Part I. Organic*. 2nd ed. revised. London: Crosby, Lockwood. 764 pp. 36s.

Liquefaction and separation of oxygen and nitrogen. R. F. MEWES and R. K. B. MEWES. U. S. 1,449,291, Mar. 20. The compressed gases, without liquefaction, are passed through a heat interchanger to cool them and led to a dephlegmating column where they are allowed to expand and ascend in contact with a descending current of liquid N, which cools the O to the point of liquefaction. Further heat interchange of gases and sepn. are subsequently effected.

Separating oxygen and nitrogen. W. A. DARRAH. U. S. 1,448,654, Mar. 13. Compressed air is passed through fused Ag to effect selective absorption of O and the associated Ag and O thus obtained are transferred as a spray while still under pressure to a chamber of lower pressure, where the O is released.

Drying colloids. G. P. LUNT. U. S. 1,450,377, Apr. 3. Smokeless powder or other colloids to be dried are heated and a current of CO<sub>2</sub>, SO<sub>2</sub> or other inert gas is passed in contact with them in a closed circuit to take up vapors repeatedly. Vapors are constantly removed from the gas at a rate so regulated as to maintain surface evapn. from the material about equal to the rate of diffusion of the solvent through the mass of the material.

Lubricating oil. E. G. ACHESON, JR. U. S. 1,448,246, Mar. 13. Unfiltered lubricating oils are standardized as to color by the addn. of small amts. of deflocculated C.

Lubricating oil from low-temperature tar. E. EICHWALD and H. E. R. VOGEL. U. S. 1,450,026, Mar. 27. A distillate from low-temp. tar is subjected to the action of an a. c. and to polymerization simultaneously to obtain a lubricating oil of good quality.

Lubricating mixtures. R. P. JUDD. U. S. 1,449,608, Mar. 27. Finely divided Zn white 10 is mixed with lubricating oil 100 parts to form a mixt. suitable for lubricating bearings of heavy machinery.

Lubricating mixture. S. A. BULLOCK. U. S. 1,449,379, Mar. 27. A compn. for lubricating metal-cutting tools is formed of a "sol. oil" 58.2, talc 38.8, Na<sub>2</sub>CO<sub>3</sub> 1.8 and H<sub>2</sub>O 1.2 parts.

Distilling lubricating oil. J. E. SCHULZE. U. S. 1,448,709, Mar. 13. Mineral oil products such as "stripped" crude oils which contain practically no constituents of the volatility of gasoline are distd. under an abs. pressure of not more than 25 mm. Hg to obtain a straight overhead lubricating oil distillate of naphthenic base oil having a viscosity of not less than 90 sec. Sayboldt at 100° and substantially free from tarry substances.

Decolorizing lubricating oils. T. F. ORR. U. S. 1,448,084, Mar. 13. Acid, preferably 98% H<sub>2</sub>SO<sub>4</sub>, is mixed with the oil by successive addns., with intermediate addn. of H<sub>2</sub>O, sludge is removed after each addn. of acid, and, after final removal of acid sludge, the oil is washed with alkali.

Synthetic gum (phenol-ketone product). J. MCINTOSH. U. S. 1,448,556, Mar. 13. A condensation product formed from a phenol and ketone, e. g., PhOH and acetone or

methyl ethyl ketone, is heated to convert it into solid form, dissolved in about half its wt. of a solvent, *e. g.*, acetone, alc. or benzine, and about 5% its wt. of a hardening agent, *e. g.*,  $(\text{CH}_3)_2\text{N}_4$ , and the mixt. is subjected to heat and pressure to convert it into an infusible product, adapted for *elec. insulation*.

**Heat insulation.** R. ILLEMANN. U. S. 1,450,856, Apr. 3. A porous insulating material adapted for covering steam boilers is prepd. by mixing calcined gypsum and an excess of  $\text{H}_2\text{O}$  and then intermittently agitating the mixt. until a plastic spongy mass is produced and finally evapg.  $\text{H}_2\text{O}$  to leave an air-filled mass.

**Insulating board.** G. H. ELLIS. U. S. 1,449,221, Mar. 20. A sheet material adapted for use as a heat insulation or foundation for plaster or stucco is formed of waste paper, straw, wood fiber or other vegetable fibers molded with a binder of liquid bitumen to form a porous, self-sustaining product.

**Electric insulating material.** G. A. BURR, J. R. McCCLAIN and L. B. FROST. U. S. 1,448,386, Mar. 13. Fibrous sheet material, *e. g.*, paper, is impregnated with insulating varnish and coated with a phenolic condensation product.

## 14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW AND G. C. BAKER

**Plant control of chlorination by the excess-chlorine method, as employed in N. Y. City's supplies.** F. E. HALE. *J. Am. Water Works Assoc.* 10, 247-64 (1923).—The excess adopted was 0.10 p. p. m. after a contact interval of 10 to 30 min. With two easily explained exceptions *B. coli* has been entirely absent from the treated water in all four plants using this excess. No noticeable increase in taste or odor has resulted. The \$30,000 increase in cost is considered well spent.

D. K. FRENCH

**Report of Committee No. 4, on Colloidal Chemistry of the Council on Standardization.** R. S. WESTON, *et al.* *J. Am. Water Works Assoc.* 10, 273-80 (1923).—The practical significance of *ph* detns. for coagulation, softening, filtration and corrosion is discussed. Properly coagulated water is frequently more corrosive. Alkali should be added after filtration to control corrosion.

D. K. FRENCH

**Determining hydrogen-ion concentration for filter-plant operation.** WM. D. HATFIELD. *J. Am. Water Works Assoc.* 10, 298-303 (1923); *cf.* C. A. 16, 4291.—Colorimetric methods for the detn. of *ph* are considered more rapid and satisfactory than calcn. from alky. and  $\text{CO}_2$  content. Many methods and indicators are discussed. For av. plant control the method of Gillespie, or its modification, which is given in detail, is preferred. Buffer solns. and permanent standards are considered.

D. K. F.

**Graphic representation of water analyses.** W. D. COLLINS. *Ind. Eng. Chem.* 15, 394 (1923).—Areas proportional to the mg. equivs. of the radicals that take part in the equil. of the system are plotted.  $\text{SiO}_2$  is represented by a black area extending across the top of both the positive and negative ion columns and suspended matter is shown by a brown or sepia area, frequently several times the combined width of the acid and basic columns. Type analyses are illustrated.

G. C. BAKER

**Certain limitations of the *Bacillus coli* method in water examinations.** V. GOVINDA RAJU. *J. Hyg.* 21, 130-3 (1922); *Pnb. Health Eng. Abstracts* April 7, 1923.—Frogs were found responsible for an increase in fecal bacilli in tanks of water. Fecal bacteria also increased on storage and passage through pipe lines. Efficiency of sand filters should be judged from samples collected from the filter well and not the storage reservoir, and where samples are collected from pipe lines consideration should be given to possible multiplication. Temp. of water is not considered.

G. C. BAKER

**Report on water.** J. W. SALE. *J. Assoc. Official Agr. Chem.* 6, 307-12 (1923).—It is recommended that the method for Ph and Zn (C. A. 16, 2563-4) be adopted as

tentative. A substitute method for Cu is recommended. Boil the moderately acid filtrate contg. Fe, Cu and Zn to remove  $C_6H_5OH$ ; adjust the vol. to 200 cc. and add 1 g.  $NH_4Cl$ . Heat to boiling, sat. with  $H_2S$ , boil to remove pptd. S, let stand 2 hrs., filter and wash the  $CuS$  with  $H_2O$  contg.  $H_2S$ . Dissolve the  $CuS$  in hot  $HNO_3$  (1 to 5), cool, add phenolphthalein, and make slightly alk. with  $NH_4OH$ . Add 10 cc. of a 10% soln.  $NH_4NO_3$ , adjust the vol. to 100 cc. and boil gently until the soln. is neutral to litmus. Filter to remove any Fe and adjust the filtrate to a vol. of 100 cc. Add to an aliquot part 3 drops  $K_4Fe(CN)_6$  soln. Compare the color with Cu standards, prepd. as follows: to a measured amt. of standard Cu soln. add phenolphthalein, a slight excess of dil.  $NH_4OH$  and 1 cc. of a 10% soln. of  $NH_4NO_3$ , boil till neutral to litmus, cool and add 3 drops of  $K_4Fe(CN)_6$ . Make color comparisons in 100-cc. Nessler jars. Additional methods for the analysis of salt are recommended for study next year.

G. C. BAKER

The chemical treatment of condensing water. L. L. ROBINSON. *Elec. Times* 61, 607-8(1922); *Science Abstracts* 25B, 579-80.—By chlorinating surface waters used for cooling purposes, algae and other gelatinous growths giving rise to troubles in condensers were inhibited. Better vacuum was maintained and less circulating water was used. The "chloronome" app. for applying  $Cl$  gas is described. G. C. B.

Kestner system for the degassing of boiler feed water. ANON. *Iron Coal Trades Rev.* 106, 84-5(1923).—A description with figs. The O is removed by finely divided steel, specially prepd. both in respect to chem. compn. and phys. condition. The advantages are: The heat in the blow-down water is conserved; the concn. of salts in the boiler is limited to a predetd. figure; salts contained in the blow-down water are usefully employed in softening the make-up water; the blow-down water itself after sepn. of the contained crystallizable salts and suspended matter is returned to the boilers; all scale-forming salts are removed outside the boiler; corrosion in the boiler, economizer, and pipe connections is eliminated. J. L. WILEY

Present-day tars for pipe coating. W. R. CONARD. *J. Am. Water Works Assoc.* 10, 304-8(1923).—Present-day tars are frequently so different from those for which the standard pipe coating specifications were written that revision is suggested.

D. K. FRENCH

Substances dissolved in rain and snow. H. S. FRIES. *Chem. News* 126, 113(1923).

W. H. BOYNTON

Microbiology and theory of activated sludge. A. M. BUSWELL AND H. L. LONG. *J. Am. Water Works Assoc.* 10, 309-21(1923).—The mechanism of the reaction in activated sludge involves converting small colloidal dispersed particles to large flocculent bodies; exptl. work seems to indicate that this is a digestive process. The org. matter after ingestion and assimilation by proper organisms is resynthesized into living material of flocculent character, in which state it will settle out. Also in *Eng. News Record* 90, 119-21(1923).

D. K. FRENCH

Determination of alkalinity in water, etc. (NOLL) 11B.

FREDERICK, R. C. and FORSTER, A.: *Public Health Chemical Analysis*. New York: D. Van Nostrand Co. 305 pp.

TOUPLAIN, F.: *Analyse générale des eaux. Constantes physiques et chimiques des eaux. Analyses de contrôle. Analyse complète des eaux. Essais divers et considérations sur les eaux minérales. Lois, décrets, règlements*. Paris: Ch. Beranger. 244 pp.

Preventing electrolytic corrosion of steam boilers. L. O. GUNDERSON. U. S. 1,449,991, Mar. 27. Electrolytic corrosion of the inner surfaces of steam boilers is pre-

vented by electrolytic deposition of As from a soln. of an arsenate which is added with the boiler feed water.

## 15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER

The catalytic action of soils. SHIGERU OSUGI. *Ber. Ohara. Inst. landw. Forsch. Japan* 2, 197-218(1922); *J. Sci. Agr. Soc.* 1922, No. 239, 241.—The investigation is divided into (1) the relation between soil catalysis and the phys. condition of soil particles, (2) the effect of chem. soil constituents on soil catalysis, (3) bacterial and enzymic actions on soil catalysis. Under part 1, 2 series of 20 pots each were filled with diff. soils. One series of pots was treated with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{HPO}_4$  and  $\text{K}_2\text{SO}_4$ , the proportions of N,  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$  being 8-6-6. The other series of 20 pots was untreated. Rice was grown in all pots. Samples of soil were taken from each pot 1 week after planting, at the time of harvest in Oct. and again in Nov. just after the pots were re-fertilized and barley was grown. The soil samples were tested for  $\text{H}_2\text{O}_2$  by titrating with 0.1 N  $\text{KMnO}_4$  after shaking 10 g. of soil with 100 cc. of 1%  $\text{H}_2\text{O}_2$  for 1 hr., and allowing the solns. to stand 48 hrs. To discover a reason for the observed changes in catalytic action, the concns. of the  $\text{H}_2\text{O}$  exts. of each sample were detd. by measuring the elec. cond. The colloid portion of the soil was detd. by shaking 30 g. of soil with 60 cc. of  $\text{H}_2\text{O}$  for 1 hr. and allowing to stand 48 hrs., the liquid was then pipetted off and dialyzed and the residue weighed and the data were calcd. per 100 g. of soil. Part 2. The catalytic action of humus, of silicic acid and of silicates, of  $\text{Al}_2\text{O}_3$  and Al silicate, of the oxide, hydroxide and phosphate of ferric Fe and of the oxide and phosphate of Mn were investigated. In Part 3 the influence of bacteria on soil catalysis was shown to be small (not over 10%). The action of enzyme or enzyme-like substances is quite remarkable and may account for 30-50% of the activity of the original soil. The remaining activity may be due to inorg. and org. soil constituents, among which  $\text{Mn}_2\text{O}_3$  is most important,  $\text{Fe}_2\text{O}_3$  next and humus least important. Soil reactions also may influence the decompn. of  $\text{H}_2\text{O}_2$ . It is shown that soils decompose  $\text{H}_2\text{O}_2$  to varying degrees. Coagulation and peptization of soil particles result in a change of magnitude of soil catalysis, the former decreasing and the latter increasing the power. Silicic acid and silicates,  $\text{Al}_2\text{O}_3$  and silicate of Al have no action on  $\text{H}_2\text{O}_2$ . F. C. COOK

Plant indicators of soil types. A. P. KELLEY. *Soil Science* 13, 411-24(1922).—Soil acidity was found to have sufficient influence on the native flora of certain soils to enable the investigator to recognize the soil type by certain indicator plants growing on it. Variation in species in certain cases is attributed to soil acidity. With some soils the acidity seems to become higher late in the summer. Rate of leaf decay, degree of slope and relative elevation have an effect upon soil acidity. R. BRADFELD

Relations between the active acidity and lime requirement of soils. E. T. WHERRY. *J. Wash. Acad. Sci.* 13, 97-102(1923).—Because of the ease with which relative values can be appreciated, it is urged that active acidity (hydrogen-ion concentration) be stated in the form of specific acidity ("S.A."). Calling lime requirement in parts per thousand of  $\text{CaO}$  "L.R.," the relation between these for a given soil may be expressed by a coefficient "C" (the initial letter of colloid) in the equation  $\text{L.R.} = \text{C} \times (\text{S.A.} - 1)$ . The value of C is believed to be a measure of the adsorptive power of the soil colloids for H-ion. Although statements in the literature suggest that C may be nearly enough constant to permit calcn. of L.R. from S.A., in 80 soils referred to in the paper, on which both have been detd., the value of C varies widely, from 0.002 to over 0.5. It is therefore impracticable to calc. L.R. from S.A. detns. in general. However, soils may perhaps be roughly classified on the basis of the value of C, a convenient ratio



between classes being  $3/\overline{10}$ ; only if some simple procedure is first devised for classifying a given soil, can there be detd. from its S.A. its L.R. E. T. WHERRY

The hydrogen-ion concentration of some Indian soils and plant juices. W. R. G. ATKINS. *Agr. Research Inst. Pusa, Bull.* 136, 12 pp. (1922).—Values of  $p_H$  are given for a variety of Indian plants. Indian soils vary from 8.9 for the calcareous silts of Bihar to 5.3 for the black peaty soils from Shillong. Certain Assam sandy soils are acid up to  $p_H$  5.4 because of presence of traces of  $H_2SO_4$  derived from the oxidation of S in the pyrites present. This accounts for the high available  $P_2O_5$ .  $CaSO_4$  will, by pptn. of  $CaCO_3$  reduce the alky. of a  $Na_2CO_3$  soln. from  $p_H$  10.0 to  $p_H$  8.0, which explains the value of gypsum on black alkali lands. H. W. EASTERWOOD

Stratification and hydrogen-ion concentration of the soil in relation to leaching and plant succession, with special reference to woodlands. E. J. SALISBURY. *J. Ecol.* 9, 220-40 (1922); *Physiol. Abstracts* 7, 206-7.—The stratification concerns chem. compn. (content of bases, org. matter, H-ion concn.) and macro- and micro-organic population. Bases increase with increasing depth, but org. matter decreases. There is a gradient of H-ion concn., the max. at the surface. The org. population decreases with depth. There is a fairly close relation between org. content and real acidity; buffer action is greatest in the layer of max. org. content. H. G.

The influence of soil reaction upon the growth of actinomycetes causing potato scab. S. A. WAKSMAN. *Soil Science* 14, 61-76 (1922).—The limiting acid reaction for the growth of *Actinomyces scabies* in culture soln., properly buffered and in soils varies with the strain. For most strains the limiting reaction is about  $p_H$  5. The saprophytic soil actinomycetes seem more acid-resistant than *A. scabies* strains. By the use of the proper amt. of S inoculated with *Theobacillus thiooxidans* an acid reaction is obtained, which will control the growth of *A. scabies* in the soil. R. BRADFIELD

The Clark hydrogen electrode vessel and soil measurements. D. J. HEALY AND P. E. KARRAKER. *Soil Science* 13, 323-8 (1922).—The use of the regular Clark H-electrode vessel for measurements of the  $p_H$  of soils is described. Air-dry soils were found to be slightly more acid than the same soils in the fresh condition. The  $p_H$  values obtained by the electrometric method were in every case considerably lower than those obtained on the same soils by the Wherry colorimetric method. R. BRADFIELD

Further studies on the soluble-salt content of field soils. C. E. MILLAR. *Soil Science* 13, 433-48 (1922).—A continuation of work previously reported (McCool and Millar, *C. A.* 13, 762) on the changes in the sol.-salt content of cropped and uncropped soils for the period March to October for the years 1919 and 1920. The concn. of sol. salts was estd. by the freezing-point depression. The sol.-salt content of the surface 6 in. of soils free from vegetation is low in early spring and late fall, but reaches a max. in the summer. The salt content of the 6-12-in. section was low throughout the season. Salts accumulated in the surface  $1/4$  in. of the uncropped soil during dry periods. Plant growth tended to prevent this accumulation. Rainfall was a factor in the accumulation and distribution of the salts but other factors had an influence. Org. matter did not increase the rate of accumulation of the sol. salts. R. BRADFIELD

Microorganisms of the soil and the fixation of atmospheric nitrogen. M. CECILET. *Rev. sil.* 58, 189-92 (1923).—A review and discussion. P. R. DAWSON

Microbiological analysis of soil as an index of soil fertility. I. The mathematical interpretation of numbers of microorganisms in the soil. S. A. WAKSMAN. *Soil Science* 14, 81-101 (1922).—A study is made of the probable errors involved in detg. the numbers of microorganisms in soils using statistical methods. The common methods yield results too variable to be very reliable. Only by the use of a large number of plates and by making an accurate detn. of the probable error involved can the proper "weight" be assigned to the results. Field samples vary widely. A large number of composite

field samples should be used. A table showing the "weight" to be attached to the detns., based on the number of plates and the number of soil samples is suggested. R. B.

**Nitrogen fixation in arid climates.** B. H. WILSDON AND BARKAT ALI. *Soil Science* 14, 127-33(1922).—Certain non-irrigated soils in the Punjab are dependent almost wholly on the natural fixation processes for their N supply. The amts. of N removed by crops indicate that about 38 lbs. of N are fixed per year. In 1916 the av. fixation in 4 different districts of the Punjab amtd. to an av. of more than 100% of the total N in the soil. The largest fixation observed since then has been 45%. The rapid fixation always follows a prolonged dry period. Rapid fixation is followed by an almost equally rapid loss. R. BRADFIELD

**Field moisture capacity and wilting point of soils.** W. L. POWERS. *Soil Science* 14, 150-65(1922).—Studies of the wilting point of various crops in the field were found to be the best guide for detg. the exact time to irrigate. The point varied with the temperature, humidity, crop and type of soil. The heaviest of normal soils had a usable water capacity of only 2 in. per acre ft. Peat retains as much as 3-4 in., silt loam  $1\frac{3}{4}$  in., fine sand 1 in., coarse sand only  $\frac{1}{2}$  in. per acre ft. The irrigation requirement is greater for soils of coarse texture and low humus content and is largely due to unavoidable waste in connection with light frequent irrigations. R. BRADFIELD

**The growth of fungi in the soil.** S. A. WAKSMAN. *Soil Science* 14, 153-7(1922).—A method is suggested for demonstrating soil fungi mycelium. Manure and acid fertilizers like  $(\text{NH}_4)_2\text{SO}_4$  increased the numbers of fungi; lime caused a decrease. R. BRADFIELD

**Occurrence of sulfides in Minnesota peat soils.** C. O. ROST. *Soil Science* 14, 167-74(1922).—Sulfides were found in general at all levels in the peat, in the muck substratum and in the upper portions of the mineral subsoil. The greatest amt. was in the lowest portion of the peat layer. The reaction of these soils was but little related to the relative amts. of sulfides present; it is controlled largely by conditions permitting oxidation of the sulfide to  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$ . The sulfide content (as  $\text{H}_2\text{S}$ ) varied from 0.016% to 0.060% in the lower layer of peat and from 0.002% to 0.013% for the muck substratum immediately beneath. Sulfides are more common in the peats of north-western Minnesota than in those of the northeastern section of the state. R. B.

**The modern trend in fertilizer-plant operation.** E. H. ARMSTRONG. *Ind. Eng. Chem.* 15, 415-6(1923).—The history of the  $\text{H}_3\text{PO}_4$  industry is reviewed and its relation to the phosphate industry discussed. A description of certain steps in the modern plant process for making acid phosphate is given. M. S. ANDERSON

**Analysis of products formed by the hydrolysis of cyanamide by acids.** A. GRAMMONT. *Bull. soc. chim.* 33, 123-8(1923).—The fertilizing value of the various products formed from  $\text{CaCN}_2$  is not expressed by the N content. Some of the products contg. N have a negative value as fertilizer. Cyanamide itself is very toxic to plants, dicyanodiamide possibly has some fertilizing value, but dicyanodiamidine is sometimes inert and sometimes toxic. In the analysis of a fertilizer contg.  $\text{CaCN}_2$  it is best, therefore, to det. (1) total N, (2) N as urea, (3) dicyanodiamidine N and (4) ammoniacal N. When the sum of the last 3 kinds of N is deducted from the total N, the difference may be assumed to represent the N of dicyanodiamide. All of the original cyanamide will, in the proposed procedure, be hydrolyzed and detd. as urea. *Detn. of total N.*—Decompose by the Kjeldahl method enough material to correspond to about 0.2 g. N, using 5 g. powdered  $\text{K}_2\text{SO}_4$  and 40 cc. of 78% concd.  $\text{H}_2\text{SO}_4$ . Boil gently for 1 hr. and then more strongly for 3 hrs. Continue as usual. *Detn. of  $\text{NH}_3$ .*—Since cyanamide derivs. may give a little  $\text{NH}_3$  when heated with  $\text{NaOH}$  it is desirable to det. the  $\text{NH}_3$  compds. of a fertilizer by transforming the  $\text{NH}_3$  into hexamethylenetetramine. To a  $\text{H}_2\text{SO}_4$  soln. contg. 0.15-0.2 g. of total N, add a few drops of phenolphthalein indicator

and titrate with dil. NaOH to a pink color. Add 10 cc. of commercial HCHO soln. and dil. with 5 or 6 vols. of water. By the reaction with HCHO each mol. of  $\text{NH}_4$  sets free 1 equiv. of H ion, which can be titrated with NaOH. *Detn. of urea*.—Use the method of Fosse which is based on the action of xanthidrol on urea. *Detn. of dicyanodiamidine*.—Use the method of Dafert and Miklomb, which is based upon the formation of the insol. Ni salt.

W. T. H.

**Composting rock phosphate with sulfur in slightly alkaline calcareous soils.** W. RUDOLFS. *Soil Science* 14, 37-59(1922).—Sulfur is oxidized in a slightly alk. calcareous soil and  $\text{P}_2\text{O}_5$  added in the form of rock phosphate is rendered more sol. Light has a slightly detrimental effect upon the organisms; a temp. of  $30^\circ$  was more favorable than room temp. The activities of the organism are stimulated during the first weeks of the incubation period by small quantities of  $\text{H}_2\text{SO}_4$ .  $\text{NaHCO}_3$  has a stimulating effect in soils low in org. matter.  $\text{AcOH}$  and  $\text{NaHSO}_4$  are slightly detrimental.  $\text{FeSO}_4$  and  $\text{Al}_2(\text{SO}_4)_3$  have no influence in concns. of 0.02%. Partial sterilizations by means of  $\text{NaCl}$  and  $\text{HCl}$  are of no value. The amt. of soil in the mixts. was reduced from 6% to 1.6% with success. It is possible to supply the bulk of the nitrogen needed in the form of  $(\text{NH}_4)_2\text{SO}_4$ . The quantity of S can be reduced to approx. the amts. used in the factory method of making acid phosphate. Sulfur oxidation nearly ceases with an abundance of air. The  $\text{pH}$  values of the mixts. are gradually reduced to about 3 and then become const.

R. BRADFELD

**Oxidation of iron pyrites by sulfur-oxidizing organisms and their use for making mineral phosphates available.** W. RUDOLFS. *Soil Science* 14, 135-46(1922).—Pyrites was attacked by microorganisms and oxidized to the sulfate form. When composted with S and rock phosphate pyrites does not interfere with the availability of the  $\text{P}_2\text{O}_5$ . Replacement of soil by  $(\text{NH}_4)_2\text{SO}_4$  in the pyrites composts produced increased amts. of sol.  $\text{P}_2\text{O}_5$ . Aeration of sulfur-pyrites rock phosphate compost mixts. by a continuous stream of moist air had little or no beneficial effect upon the production of acidity unless  $(\text{NH}_4)_2\text{SO}_4$  was added.

R. BRADFELD

**Arsenic, a catalytic fertilizer.** C. PICADO. *Compt. rend. soc. biol.* 87, 1338-9(1922).—Expts. were made with soil, one sample of which was used alone while to the other 0.1 g. of  $\text{As}_2\text{O}_3$  was added per 100 kg., and the 2 were spread out over a surface of 1 sq. m. Corn was planted in both samples of soil; the crop in the second was 77% heavier than in the first (control). Expts. with varying quantities of  $\text{As}_2\text{O}_3$  showed that 1 kg. per 1 hectare of soil was enough to produce favorable results and that it was not necessary to go beyond 8 kg. of  $\text{As}_2\text{O}_3$  per hectare. In the concn. in which the As is present in the soil thus treated it exercises no bactericidal action, but tests with sterile soil and sterilized seed show that the larger yield is even then obtained from the soil treated with As, which is thought to be indispensable for the growth of plants.

S. MORGULIS

**Nitrogen fertilization of lucerne.** PAUL WAGNER. *Mitt. deut. Landw.-ges.* 38, 49-51(1923).—Field and plot expts. were carried out with lucerne, with varying amts. of N as  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NaNO}_3$  in addition to const. amts. of  $\text{P}_2\text{O}_5$  and  $\text{K}_2\text{O}$ . The yields of 3 sep. harvestings are given. In no case was the increase in yield sufficient to offset the cost of the N fertilizer, and in a number of cases the yields were less than with no N. In all cases the use of N fertilizers slightly depressed the N content of the harvested crop.

K. D. JACOB

**Pot cultures with barley in soil from a long-time fertilizer experiment.** A. R. C. HAAS. *Botan. Gaz.* 75, 95-102(1923).—The data presented show the lack of agreement between the barley-producing power of soils and the yield and condition of citrus on such soils at the time the samples were taken. The amt. of nitrogen previously added to a soil is not an accurate measure of its barley-producing power. The addition of

phosphoric acid or potash to the soils studied has not shown any added advantages for the growth of barley or of citrus.

BENJAMIN HARROW

**Contribution to the knowledge of the nutrition of fabaceous plants.** M. GERLACH AND O. NOLTE. *Mitt. deut. Landw.-ges.* 38, 78-80(1923).—During the early growing period of fabaceous plants the N supply is drawn from the protein of the seed and the easily assimilable N compds. of the soil. After the young plants have exhausted the supply of N from these sources and before the N-fixing bacteria in the root nodules begin functioning there usually exists a period of N starvation. The application of com. fertilizers furnishes a steady supply of N during this period and should result in somewhat increased yields, as indicated by a number of expts. with peas, red clover and lucerne.  $\text{NaNO}_3$  and urea gave the best results followed by stable manure and  $(\text{NH}_4)_2\text{SO}_4$ . In all cases, the increases in yield were slight. With lupines  $(\text{NH}_4)_2\text{SO}_4$  gave lower results than with no N. The value of  $\text{P}_2\text{O}_5$ ,  $\text{K}_2\text{O}$  and lime as fertilizers for fabaceous plants is pointed out.

K. D. JACOB

**Increasing the crop yield by efficient disinfection of the seed.** APPEL. *Mitt. deut. Landw.-ges.* 38, 37-9(1923).—A general discussion of the prevention of certain plant diseases by disinfecting the seed previous to planting. The chem. compds. and app. used are briefly described and their relative merits indicated.

K. D. JACOB

**The "oleoresin" of pyrethrum and soap-pyrethrum.** A. JUILLET. *Rev. vit.* 58, 169-76(1923).—A review and discussion.

P. R. DAWSON

COMPARDOU, J.: *Le tetraphosphate*. Toulouse: E. H. Guillard. 72 pp.

FRANK, ADOLF: *Ausgewählte Vorträge und Schriften über Kalisalz, Kalkstickstoff, Moorkultur u. Torfverwertung, Zellstoffgewinnung, Mosaikindustrie u. s. w.* Berlin: M. Krayn. 291 pp.

FREYBE, OTTO: *Der Chemische Unterricht an landwirtschaftlichen Schulen auf der Grundlage von Anschauung und Versuch. II.* Berlin: P. Parey. 96 pp.

KWISDA, A.: *Kunstdünger, Handelsdünger*. Vienna: Waldheim-Eberle. 111 pp. M 150.

LYON, T. L. and BUCKMAN, H. O.: *The Nature and Properties of Soils*. New York: Macmillan Co. 588 pp. Reviewed in *Expt. Sta. Record* 47, 317(1922).

**Fertilizer.** YOSHISABURO KIDA and KITARO WATANABE. Japan. 40,427, Oct. 25, 1921. The fertilizer is a mixt. of a viscous soln. of hair or leather dust in  $\text{H}_2\text{SO}_4$  (50-55 Bé.), gypsum contg. free  $\text{H}_3\text{PO}_4$  and powd. bone. In mixing,  $\text{Ca}_3(\text{PO}_4)_2$  in the material is converted into  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

## 16—THE FERMENTATION INDUSTRIES

C. N. FREY

**Preservative principles of hops.** I. F. L. PYMAN, HAROLD ROGERSON and T. K. WALKER. *J. Inst. Brewing* 28, 929-34(1922).—Attempts were made to isolate cryst. hop-bitter acids by fractional extrn. with alkalies of increasing strength of an ethereal soln. of the soft resins, obtained by extrn. of ground hops with light petroleum. Lupulone was isolated in small yield in colorless prisms, m. 94.5-95.5°. No humulone was obtained by this method, and the only other cryst. compds. isolated were lactic acid,  $\text{C}_{16}\text{H}_{30}\text{O}_2$ , a satd. fatty acid previously found only in the fungus *Agaricus integer*, and small quantities of the constituents of the wax, hentriacontane, ceryl alc., and cerotic acid.

J. C. S.

**Physico-chemical methods in brewery laboratories.** W. DIETRICH. *Woch. Brau.* 39, 232-3(1922).—The limitations of purely chem. methods are pointed out.

and stress is laid on the value of the information given by modern methods of phys. chemistry. J. S. C. I.

**Determination of diastatic power.** W. WINDISCH, W. DIETRICH AND P. KOLBACH. *Woch. Brou.* 39, 213-4, 219-22, 225-6(1922).—The divergent values for the diastatic power of a malt obtained by the iodometric method when different starches are used depend to some extent on variations in the H-ion concn. and degree of dispersion of the starch solns. Since the malt exts. obtained from different malts vary but slightly in acidity and since also but little of the ext. is used in detg. the diastatic power, the value of  $p_H$  for the mixt. of starch soln. and malt ext. depends almost entirely on the acidity of the starch. Samples of sol. starch supplied by different makers gave 2% (on dry matter) solns. varying in  $p_H$  from 3.7 to 6.2, the values after addn. of one and the same cold-water malt ext. ranging from 4.1 to 6.1 and the nos. obtained for the diastatic power from 126 to 95 (or for a second malt, from 133 to 95). When the values of  $p_H$  were made equal in all the cases to 4.9 by addn. of a buffer soln., the diastatic powers found varied only from 124 to 113 (131 to 121). One of the starches gave lower values for the diastatic power after addn. of the buffer soln. owing to the fact that the optimum value of  $p_H$  for diastatic action is not 4.9, as stated by Adler, but 4.26. Although the activity of diastase is not appreciably less for  $p_H$  5.8, which is the av. value for unboiled wort, than it is for  $p_H$  4.3, adjustment of the H-ion concn. may result in increases of the yield of ext. in the brewery by as much as 2%. This increase is due to the fact that increase of the acidity (to  $p_H$  5) favors the action of the proteolytic enzymes and hence not only renders a greater proportion of the proteins permanently sol. but also renders the starch granules more readily accessible to the action of the diastase. The increased acidity also lowers the danger of subsequent protein turbidity, produces a better "break" of the wort, and improves the flavor of the resulting beer. A method of detg. diastatic power, in which the I used by the starch and the  $p_H$  value of the starch soln. are taken into account, is described. The same starch must be employed in all cases, Kahlbaum's sol. starch being recommended; the starch soln. must be prepd. in a definite way and, since the course of the conversion depends on the degree of dispersion, must be used fresh. By addn. of a suitable quantity of a buffer soln. contg. NaOAc and AcOH, the  $p_H$  of the soln. is brought to  $4.3 \pm 0.1$ . Details of the procedure and of the method of calcn. of the results are given. J. S. C. I.

## 17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

**General studies of cinchona.** J. PIERAERTS. *Bull. agr. Congo Belge* 13, 628-62 (1922).—The cinchona tree has been introduced into the Belgian Congo and grows successfully. A summary of analyses is given showing the content of cinchonidine, quinine, and other alkaloids in various species grown in different places. M. S. A.

**Ethyl alcohol as stabilizer of hydrogen peroxide.** LISIEVICI-DRAGANESCU. *Bul. soc. chim. Romania* 4, 65-8(1923).—To maintain the strength of  $H_2O_2$  as a powerful antiseptic the following substances have been suggested:— $H_2SO_4$ , AcOH, chloral,  $CHCl_3$ , glycerol, naphthalene, phosphoric and boric acids, benzene, NaCl, acetanilide and EtOH. Using com.  $H_2O_2$  which furnishes O to the extent of 10 times its vol. and "perhydrole" which furnishes 100 times its vol. of O a series of tests were run, the alc. content and light conditions being varied. Results show that EtOH is a very good preservative, when added in the proportion of 10% to ordinary com.  $H_2O_2$  and 30% to "perhydrole," the O titer remaining const. for 4 months. HOWARD E. BAYSFORD

**A delicate reaction of neoarsphenamine.** K. SCHERINGA. *Pharm. Weekblad* 60, 248(1923).—Neoarsphenamine in dilns. as great as 1-1000 gives a distinct violet color-

tion with a concd. soln. of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . The reaction is, however, not specific. Pyramidone gives a purple color, aniline a deep blue,  $\alpha$ -naphthylamine a blue, brucine a red; and  $\text{PhNH}$  a green color. Arsphenamine also gives a violet coloration but the reaction is less sensitive than that of neoarsphenamine. A. W. DOX

**Some drug-store and laboratory experiences.** D. J. DE JONG. *Pharm. Weekblad* 60, 315-26(1923).—In the examn. of gum arabic, cantharides, creosote, glycerol, Ca lactate, xeroform and santonin, the tests prescribed by the Dutch Pharm. were found to be inadequate. E. g., the gum arabic contained rosin and still conformed to the standard, and the Ca lactate contained Ba, which the Pharm. does not take into account. Observations regarding the effect of light on Dakin soln. and on  $\text{KMnO}_4$  soln. are also recorded. A. W. DOX

**Fats, oils and waxes in current use in pharmacy.** CL. GENOT. *J. pharm. Belg.* 5, 73-5, 89-92, 105-7, 121-4, 137-9, 153-6, 173-6(1923).—G. discusses the source, methods of extrn., properties, compn., tests, adulterations and uses of the following: cacao butter, expressed oil of laurel, expressed oil of almonds, olive oil, colza oil, peanut oil, linseed oil, poppy-seed oil, castor oil, croton oil, sesame oil, beeswax, spermaceti, lard, wool fat, cod-liver oil, paraffin (solid), paraffin (soft) and paraffin (liquid). A. G. DUMÉZ

**Matriculation sheets.** A. SCHAMELHOUT. *J. pharm. Belg.* 5, 97, 98, 112, 164 (1923).—Monographs intended for introduction into the Belgian National Formulary are presented for the following: tropacocaine hydrochloride, yohimbine hydrochloride, zinc tannate and zinc acetate. A. G. DUMÉZ

**Jottings from a pharmaceutical laboratory note book.** GEORGE E. EWE. *Pract. Drug.* 41, No. 3, 22-3(1923); cf. C. A. 17, 449.—*Production of refined cresol for serum preservation.*—Com. cresol is dissolved in a 5% soln. of NaOH (1 lb. of cresol to 1 gal. of NaOH soln.), the undissolved hydrocarbons are sepd. and the soln. is filtered. The cresol, liberated with  $\text{H}_2\text{SO}_4$ , is fractionated in a glass-lined still equipped with a dephlegmator and a glass-lined or block-tin condenser. Re-fractionation may be necessary to obtain a satisfactory product. By agitating the filtered alk. soln. thoroughly with  $\text{CCl}_4$  or  $\text{C}_6\text{H}_6$  ( $\frac{1}{2}$  pint of solvent to 1 gal. of soln.), sepg. and drawing off the cresol soln., liberating the cresol with  $\text{H}_2\text{SO}_4$  and fractionating, re-fraction is usually not necessary. The best grades of refined cresol are those which produce a minimum coloration or turbidity when autoclaved with normal saline soln. *Application of casein to detergent purposes.*—Casein, rendered sol. by treatment with an alkali, is more effective as a detergent than the fatty acid soaps. For practical use it must be mixed with one of the latter (about 25 parts of casein detergent paste to 75 parts of fatty acid soap). A mixed soap of this nature is suggested for use by surgeons because of its strikingly rapid and efficient detergent properties. Formulas for making various soaps, including a germicidal soap, are given. A. G. DUMÉZ

**Genesis of camphor.** A. GAWALOWSKI. *Pharm. Monats.* 4, 21(1923).—A discussion of the rather loose nomenclature obtaining in certain quarters relative to the products Japan and Borneol camphors as opposed to synthetic  $(\text{C}_{10}\text{H}_{16}\text{O})$  and artificial  $(\text{C}_{10}\text{H}_{17}\text{Cl})$  = terpinhydrochloride) camphors. W. O. E.

**Microchemical detection of fraxin in the plant.** HERMINE GERBERS. *Pharm. Presse* 28, No. 1, 2-3; No. 2, 2-3(1923).—Three reactions are described, which are calcd. to demonstrate the presence of this glucoside. The 1st is a general or group reaction showing fluorescence in a section of the bark placed on an object glass in a drop of  $\text{H}_2\text{O}$ , especially when viewed in reflected light against a dark background, the glass being held over an open  $\text{NH}_3$  bottle. The 2nd is a specific reaction for fraxin (in the presence of esculin). A section of bark in a drop of 20%  $\text{H}_2\text{SO}_4$  on a watch glass is heated about 20 sec. until the liquid just boils. After 24 hrs. at about  $30^\circ$ , characteristic crystals

of fraxin will have sepd. in the form of plates, striated and with rectangular indentations. The 3rd reaction, microsublimation, though not specific for fraxin offers a simple method for localizing the glucoside in the tissues. W. O. E.

**Extractum helladonnae instead of Extractum fungi secalis**—a typical substitution of medicaments. OSKAR KOPITZKY-RECHTERG. *Pharm. Presse*, 27, No. 20, 2-3 (1922).—Three cases are cited with attendant phenomena, together with suggestions for their avoidance. W. O. E.

**Medicinal plant culture.** WOLFGANG HIMMELBAUR. *Pharm. Presse* 27, No. 21, 1-2; No. 2, 2-3 (1922).—Historical, including some practical suggestions on modern cultivation. W. O. E.

**Substitution of Sorbus aucuparia for cortex frangulae.** M. JOACHIMOWITZ. *Pharm. Presse* 27, No. 24, 1-2 (1922). W. O. E.

**Maximum dose of papaverine and maximum doses of the pharmacopeia.** R. WASICKY. *Pharm. Presse* 27, No. 15; No. 16, 1-2 (1923).—A discussion of the dosage of papaverine and certain other potent drugs, with especial reference to the widely varying effects produced depending upon their different modes of administration, whether oral or subcutaneous, a fact worthy of greater consideration in the formulation of pharmacopoeial doses. W. O. E.

**Effect of mildew on the alkaloidal content of hyoscyamus leaves.** B. PETER. *Pharm. Zentralhalle* 64, 122-3 (1923).—Expts. covering 2 years' observation show that the alkaloidal content of infected leaves is about  $\frac{1}{2}$  that of the unaffected product. W. O. E.

**Liquor formaldehydi saponatus.** P. BOHRISCH. *Pharm. Zentralhalle* 64, 131-3 (1923).—Results of analysis of 4 different samples are reported. W. O. E.

**A study of Stenocalix pitanga (Berg) or Eugenia pitanga (Berg-Arech).** VÍCTOR COPPERTI AND MATÍAS GONZÁLEZ. *Anales soc. españ. fis. quim.* 20, 406-19 (1922).—This shrub, a member of the family Myrtaceae, is a native of Uruguay and is known locally as *pitanga* or *nañgapiñé*. A tea made from the young leaves and an alc. liquor flavored with the leaves and fruits are used as local remedies for all disorders of the digestive tract. The leaves contain no alkaloids, glucosides, or bitter or neutral substances of medicinal value. What valuable properties the drug has are due to a volatile oil present in the leaves to the extent of 0.4-0.5%. The oil contains citronellal, geraniol, geranyl acetate, cineol, terpinene, and various sesquiterpenes, resins, etc. Extensive analytical data are given. L. E. GILSON

**E. A. Merck.** ANON. *Chem.-Ztg.* 47, 233 (1923); *Z. angew. Chem.* 1923 (*Chem. Ind.*) 161-2.—Obituary. E. H.

**Essential oils.** SCHIMMEL & Co. *Rept. Schimmel & Co.* 1922, 5-166.—Descriptions are given of a no. of essential oils, many of which have already appeared. Essential oil from *Abies pindrow* (Indian silver fir) has  $d_{15}^4$  0.8647,  $[\alpha]_D^{20}$   $-10^\circ 59'$ ,  $n_D^{20}$  1.47328, acid no. 0.3, ester no. 6.5. Indian baldrian oil has  $d_{15}^4$  0.9361,  $[\alpha]_D^{20}$   $-34^\circ 6'$ ,  $n_D^{20}$  1.48712, acid no. 37.3, ester no. 39.8, acetyl no. 69.1. Essential oil from *Erigeron canadense* has  $d_{15}^4$  0.8720,  $[\alpha]_D^{20}$   $+53^\circ 56'$ ,  $n_D^{20}$  1.49922, acid no. 0.3, ester no. 63.5, acetyl no. 70.3. Pine needle oil from *Tsuga canadensis* has (Cable, *C. A.* 16, 2578)  $d_{15}^{20}$  0.9020-0.9234,  $[\alpha]_D^{20}$   $-14.80^\circ$  to  $21.65^\circ$ ,  $n_D^{20}$  1.4691-1.4704, acid no. 0.33-0.71, ester no. 103.8-147.35, acetyl no. 113.5-171.94. Essential oil from *Tsuga heterophylla* has  $d_{15}^{20}$  0.8444-0.8521,  $[\alpha]_D^{20}$   $-6^\circ$  to  $-20^\circ$ ,  $n_D^{20}$  1.4790-1.4840, acid no. 2.57-3.4, ester no. 6.7-17.25, acetyl no. 19.6-33.4. Spanish oil of thyme has  $d_{15}^4$  0.9297,  $[\alpha]_D^{20}$   $+0^\circ 35'$ ; it contains 45% of thymol, also amyl alc., amylcarbinols,  $\Delta^8$ -hexenol, and a new terpene,  $C_{14}H_{18}$ , of carrot-like odor, b.  $155-6^\circ$ , with  $d_{15}^4$  0.8533-0.8537,  $[\alpha]_D^{20}$   $+4^\circ 50'$  to  $4^\circ 50'$ ,  $n_D^{20}$  1.46201-1.46231. The latter compd. gives a nitroso chloride which decomposes at about  $85^\circ$ , a nitrolipide, m.  $194-5^\circ$ , and a nitrol-amine, m.  $105-8^\circ$ . The oil also contains camphene,

$\alpha$ -pinene,  $\beta$ -cymol,  $\gamma$ -terpinene, linalool, *l*-borneol,  $\gamma$ -terpineol, geraniol, and caryophyllene. Essential oil from *Cicuta virosa*, L., has  $d_{15}$  0.8909,  $[\alpha]_D^{20} + 16^{\circ}32'$ ,  $n_D^{20}$  1.4848, acid no. 3.7, ester no. 17.7.

J. C. S.

**Colchicine, its assay, isolation and special properties.** R. C. DAVIES AND J. GRIER. *Pharm. J.* 109, 210-1 (1922); cf. *C. A.* 15, 3894.—To isolate pure colchicine (*C*) in quantity, exhaust seeds and corms with methylated alc. at reflux, evap. the alc., ext. fat with ligroin, then the impure *C* with  $\text{CHCl}_3$ , evap. and dissolve in  $\text{H}_2\text{O}$ , then ppt. with phosphotungstic acid (*A*), best in presence of 0.5%  $\text{HCl}$  and 2%  $\text{NaCl}$ , wash off  $\text{NaCl}$  with 0.1%  $\text{HCl}$  and decompose the yellow, granular ppt. with  $\text{CHCl}_3$  and  $\text{NH}_4\text{OH}$ , evap.  $\text{CHCl}_3$ , take up with 50%  $\text{EtOH}$  and dry on plates. The yellow, pure product, m.  $144^\circ$  is completely sol. in  $\text{H}_2\text{O}$ . A less pure, light brown *C*, m.  $140^\circ$ , is obtained from the tartrate in 10% alc. soln.; add excess of  $\text{Pb}(\text{NO}_3)_2$ , ppt. *Pb* with dil.  $\text{H}_2\text{SO}_4$ , and ext. with  $\text{CHCl}_3$ . For volumetric detn., gradually add Mayer's reagent in 2%  $\text{H}_2\text{SO}_4$  soln., sepg. the ppt. by centrifuging. One cc. 0.05 *N* reagent = 0.011 g. *C* (Merck) (0.0147 g., A. B. Lyons). Or use reagent *A* (Scheibler's) in 1.5%  $\text{H}_2\text{SO}_4$  soln. For gravimetric detn., use *A* as in the above prepn. of *C* and ignite the ppt. The mol. ratio of *C*:*A* is 4:1; or 1:3.3 by wt. (cf. *C. A.* 14, 3041). A colorimetric method (cf. *C. A.* 6, 1340) is based on the greenish yellow tint caused by 1 drop in excess of 0.1 *N*  $\text{KOH}$  in solns. of *C* above a 0.008% limit of concn. The solubilities, chem. reactions and color tests of *C* are given.  $\text{Et}_2\text{O}$  contg.  $\text{SO}_2$  forms a canary-yellow ppt.;  $\text{PhOH}$ , cresol, thymol, tannic and salicylic acids give ppts. with *C*, indicating that in the forming of these "salts" the  $\text{OH}$  group is involved. The prepn. of the unstable salicylate and that of the more stable tannate are described. The analgesic properties of *C*, analogous to those of acetanilide etc., are due to the group  $\text{MeCONH-}$ .

S. WALDBOTT

**Peralga.** ANON. *J. Am. Med. Assoc.* 80, 942 (1923).—Peralga is sold by Schering and Glatz. It is claimed to be "a new synthetic analgesic" in which "the soundly established, rational, pain-relieving properties of amidopyrine have been chemically potentiated by the highly valued sedative properties of diethyl barbituric acid, while the hypnotic effect of the latter has been eliminated." The product is a yellow powder having a methyl amino odor. On extr. by  $\text{CHCl}_3$  from a soln. in  $\text{NaOH}$  and evapn. of the solvent, 72% of residue was obtained which was identified as amidopyrine. By soln. in 0.2%  $\text{HCl}$  a ppt. is given which was identified as barbital. The amt. recovered was 26.1%. A specimen of Peralga and a mechanical mixt. of amidopyrine and barbital were tested pharmacologically on cats. No differences could be detected. A mechanical mixt. of amidopyrine and barbital m.  $100^\circ$  with formation of a yellow color and an amino odor.

L. E. WARREN

**Caution in use of mercurochrome-220 soluble.** C. C. STOLZ. *J. Am. Med. Assoc.* 80, 1023 (1923).—An injection of a 5% soln. of mercurochrome-220 sol. into the bladder followed by a 2% soln. of procaine gave a voluminous red ppt. which had to be removed by lavage with  $\text{Na}_2\text{CO}_3$  soln. through a catheter.

L. E. WARREN

**Incompatibility of mercurochrome-220 soluble with local anesthetics and alkaloïds.** J. E. WARREN. *J. Am. Med. Assoc.* 80, 1091 (1923).—Following Stolz' observation (cf. preceding abstr.) expts. were conducted to det. the incompatibilities of mercurochrome-220 sol. with local anesthetic substances and with alkaloïds and their derivs. All solns. were 2% in  $\text{H}_2\text{O}$ , the scantily sol. local anesthetics being made sol. by a few drops of dil.  $\text{HCl}$ . Mercurochrome 220 sol. gave ppts. with each of these substances: alypine, apothesine, benzocaine, butyn, cocaine- $\text{HCl}$ ,  $\beta$ -eucaine lactate, phenacaine, procaine, propaesin, quinine and urea- $\text{HCl}$ , tropacocaine- $\text{HCl}$ , and stovaine. The ppt. in each case was of a deep red color, was amorphous and did not become cryst. on standing. In some instances analysis of the dried ppt. showed that it contained all of the essential constituents of the mercurochrome radical, i. e.,  $\text{Br}$ ,  $\text{Hg}$  and the eosin



dye substance, but that it did not contain Na or the acid radical with which the basic substance was originally combined. The ppts. were too sol. to be of value in quant. seps. of the local anesthetics but were sufficiently insol. to render dangerous the concomitant prescribing of the local anesthetics with mercurochrome-220 sol.  $\text{BzOH}$  and saligenin did not give ppts. Most vegetable alkaloids and their derivs. gave ppts. Red ppts. were given by aconitine-HCl, apomorphine-HCl, atropine- $\text{H}_2\text{SO}_4$ , brucine-HCl, cephaeline-HCl, cinchonidine- $\text{H}_2\text{SO}_4$ , cinchonine- $\text{H}_2\text{SO}_4$ , codeine- $\text{H}_2\text{SO}_4$ , diacetylmorphine-HCl, emetine-HCl, ethylhydrocupreine-HCl, ethylmorphine-HCl, gelsemine-HCl, homatropine-HCl, hydrastine-HCl, morphine- $\text{H}_2\text{SO}_4$ , narceine-HCl, narcotine-HCl, nicotine-HCl, papaverine-HCl, physostigmine salicylate, pilocarpine- $\text{HNO}_3$ , quinidine- $\text{H}_2\text{SO}_4$ , quinine-HCl, sanguinarine-HCl, solanine-HCl, sparteine- $\text{H}_2\text{SO}_4$ , strychnine- $\text{H}_2\text{SO}_4$ , and thebaine-HCl. Caffeine, colchicine-HCl, conine-HCl, methylatropine-HBr, theobromine Na salicylate and theophylline Na acetate did not give ppts.

L. E. WARREN

The effects of large doses of *Cannabis indica*. ALBERT SCHNEIDER. *J. Am. Pharm. Assoc.* 12, 208-14 (1923).—Insofar as possible S. describes the symptoms following the ingestion by himself of 3, 4, 3 and 8 cc. at different times of fluidext. of cannabis. The pulse and respiration were not greatly influenced. The effects on the neutral state (described in detail) were exceedingly variable. The diuretic action was marked in each case. Because cannabis is a drug of such uncertain and unreliable action it should be deleted from the U. S. P. It is inferior as an hypnotic. It is not analgesic but tends to amnesia and forgetfulness. Nothing in these tests explains the homicidal mania observed in Hindoo addicts. It neither stimulates nor paralyzes the higher faculties, nor does it stimulate the lower or animal faculties. It produces some sex imagery.

L. E. WARREN

#### The active principles of some South African plants (JURITZ) 11D.

GASTON, P.: *Formulaire cosmétique et esthétique*. 2nd Ed. Paris: Baillière et fils. 313 pp.

Carvacrol and thymol. R. H. MCKEE. U. S. 1,449,121, Mar. 20. Spruce turpentine is treated with fuming sulfuric acid to produce 1,2,4 and 1,3,4 sulfonic acids which are then (in the form of salts) treated with NaOH and fused to produce carvacrol and thymol.

Medicinal mixture. R. SANSEVERO. U. S. 1,449,299, Mar. 20. A compn. for local treatment of venereal diseases is prepd. from solargentum (Squibb), Na glycolcholate and  $(\text{CH}_3)_4\text{N}_4$ .

Amino compounds of cinchona alkaloids and their derivatives. C. F. BOEHRINGER & SOEHNLE. Ger. 335,113. Cinchona alkaloids which contain a free phenol hydroxyl group are coupled with diazonium salts, the azo compds. thus obtained reduced by the usual methods, and the resulting amino derivs. of the alkaloids alkylated on the phenol hydroxyl groups. *Aminoethylhydroquinine* obtained from hydrocupreine-azobenzenesulfonic acid by way of aminohydrocupreine corresponds with the amino compd. obtained by reduction of nitroethylhydrocupreine (Ger. pat. 283,537). *Cupreine-azobenzenesulfonic acid* is obtained from cupreine and *p*-diazobenzenesulfonic acid in alk. soln.; the sodium salt crystallizes in hexagonal tables with 6 mols. of water; the free acid crystallizes in red, prismatic tables with 3 mols. of water of the compn.  $\text{C}_{22}\text{H}_{26}\text{O}_4\text{N}_2\text{S}$ ; m. 257° (decompn.). *Aminocupreine*,  $\text{C}_{19}\text{H}_{24}\text{O}_3\text{N}_2$ , is obtained by reduction of cupreine-azobenzenesulfonic acid by  $\text{NaHSO}_3$  in alk. soln., and forms yellow crystals, m. 195° (decompn.), unstable like *o*-aminophenol, and forms 4 series of salts; gives by catalytic reduction *aminohydrocupreine*. The latter gives, with  $\text{EtSO}_4$  in alk. soln., *amino*

*ethylquinine*,  $C_{21}H_{27}O_4N_3$ , which forms rectangular, prismatic needles or tables like cholesterol; m. 213–14°. The monosulfate is almost colorless and the disulfate red. By catalytic reduction, *aminoethylhydroquinine* is obtained. J. C. S.

**Derivatives of hydrastinine.** K. W. ROSENMUND. Ger. 336,153. Instead of alkylidenecamines, from  $CH_2O$  and piperonylisopropylamine (cf. Ger. pat. 320,480), compds.

of the general formula  $CH_2 \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} C_6H_5 \cdot CH_2 \cdot CHR \cdot NR' \cdot CH_2 \cdot OH$  (R = hydrogen or methyl, R' = hydrogen or alkyl) are treated with catalysts. *Piperonylisopropylaminomethanol* prepd. from the base and chloromethyl alc., a colorless sirup, is heated with 10% HCl for half an hour at 100°, whereby 3-methyldihydronorhydrastinine is obtained. The hydrochloride m. 232°; the hydride m. 217°. *Homopiperonylmethyl-*

*aminomethanol*,  $CH_2 \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} C_6H_5 \cdot [CH_2]_n \cdot NMe \cdot CH_2 \cdot OH$ , obtained from the base and chloromethyl alc., is a sirup which gives on heating with 10%  $H_2SO_4$  *dihydrohydrastinine*. From *homopiperonylethylaminomethanol*, a colorless, unstable sirup, by heating with 12% HCl, *N-ethyl-dihydronorhydrastinine hydrochloride* is obtained in white needles. By the action of chloromethyl alc. on the secondary base, *piperonylisopropylmethylaminomethanol* is obtained, a colorless sirup, resinifying on warming, which gives on heating with HCl 3-methyldihydrohydrastinine hydrochloride; needles, m. 230–2°. J. C. S.

**Arsenic compounds of the pyrazolone series.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING. Ger. 313,320. Acid groups are introduced into the amino groups of compds. of the type 1-*p*-arsenodiarlyldi(4-amino-2,3-dialkyl-5-pyrazolone). The compds. thus formed, although not markedly poisonous, are strongly bactericidal and may be used in the form of their alkali salts. The products are yellow powders, decomposed by heating with acids. 5-Chloro-3-methylpyrazole-1-benzene-4'-arsinic acid is obtained by diazotization of 5-chloro-3-methylpyrazole-1-*p*-aminobenzene, treatment with arsenites, and subsequent acidification; it forms crystals, m. 192–5°, when quickly heated, with the formation of an anhydride and subsequently solidifies on elimination of water; it decomposes completely above 290°. 3-Methyl-5-pyrazolone-1-benzene-4'-arsinic acid is prepd. by diazotization of *p*-aminophenylarsinic acid, reduction, and condensation with Et acetoacetate; it crystallizes from hot water and forms a yellow *nitroso* compd. 2,3-Dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid is formed by the methylation of 3-methyl-5-pyrazolone-1-benzene-4'-arsinic acid or the corresponding 5-chloro-pyrazole deriv.; it crystallizes from water. By acting on it with  $NaNO_2$  and dil.  $H_2SO_4$ , 4-nitroso-2,3-dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid is obtained; it is bluish green and very unstable; by reduction, 1-*p*-arsenodiphenyldi(4-amino-2,3-dimethyl-5-pyrazolone) is obtained. The hydrochloride forms yellow crystals. The monoacetate, prepd. by the action of bromoacetic acid, is a yellow powder. With excess of bromoacetic acid, a *diglycine* is obtained similar to the monoglycine. By the action of formaldehyde sulfoxylate on 1-*p*-arsenodiphenyldi(4-amino-2,3-dimethyl-5-pyrazolone) hydrochloride or 4-nitroso-2,3-dimethyl-5-pyrazolone-1-benzene-4'-arsinic acid, 1-*p*-arsenodiphenyldi(4-amino-2,3-dimethyl-5-pyrazolone)monomethylenesulfoxylic acid is obtained as a yellow powder. A dimethylenesulfoxylic acid is obtained when a large excess of formaldehydesulfoxylate is used. By treating 1-*p*-arsenodiphenyldi(4-amino-2,3-dimethyl-5-pyrazolone) hydrochloride with  $NaHSO_3$  and  $CH_2O$  the corresponding 4-*N*-methyl-sulfonic acid compd. is obtained as a yellow powder. J. C. S.

**New guaiacol compounds.** PHARMAZEUTISCHE INDUSTRIE G. M. B. H. and RUDOLF HAUSCHKA. Austrian 86,131.  $SiCl_4$  or other reactive Si compd. is allowed to react with guaiacol. From  $SiCl_4$  and guaiacol, *dichlorodiguaiacetylsilicmethane*,  $SiCl_2(O-$

$C_4H_4(OMe)_2$ , and *tetrauguaiacylsilicomethane*,  $Si(O.C_6H_4OMe)_4$ , are obtained and can be partly sepd. by distn. in a vacuum. The former is a viscid substance, but by soln. in ether and evapn. can be obtained in colorless or greyish green crystals; it is slowly decomposed by water with sepn. of silicic acid. The latter is a viscid liquid which by long heating in a vacuum gives off guaiacol vapor and forms *polyguaiacylsilicon*,  $Si_3(O.C_6H_4.OMe)_{23}$ , a thick, honey-like sirup,  $b_{20}$  220°. J. C. S.

A derivative of thebaine. EDMUND SPEYER, ELSE FREUND, WALTER FREUND, HELMUTH FREUND AND LISELOTTE FREUND. Ger. 338,147. Thebaine in aq. alc. soln. is treated with an excess of mol. H, with colloidal metallic catalysts of the Pt group. E. g., to a cooled soln. of thebaine in 96% EtOH equal quantities of water and a Pd sol (1 cc. = 0.0025 g. of Pd) are added, and the mixt. is shaken in an atm. of H until no further absorption takes place. The Pd is then pptd. and the EtOH distd. off. After addn. of  $NH_4OH$ , the residue is extd. with  $CHCl_3$ . The oil remaining after evapn. of the  $CHCl_3$  is triturated with EtOH and a *hydrochloride*,  $C_{18}H_{23}O_2N.HCl$ , prepd. by the action of HCl in alc. soln.; it forms crystals, m. 310° (decomp.). The free base,  $C_{18}H_{23}O_2N$ , crystallizes in leaflets (from alc.) and m. 145–50°. It is pptd. from solns. of its salts by excess of  $Na_2CO_3$  or  $NH_3$ . With an excess of alkali the base is redissolved; it is thus amphoteric in character. In these properties and in its stability in the presence of mineral acids, the compd. described differs from tetrahydrothebaine,  $C_{18}H_{23}O_2N$  (Oldenberg, C. A. 7, 3198; Braun, C. A. 8, 3303). It contains one methoxyl group and has the characteristics of a ketone. J. C. S.

Allyl *p*-aminobenzoate. SOC. ANON. POUR L'INDUSTRIE CHIMIQUE À BALE. Swiss 92,300; cf. Adams and Volwiler, C. A. 15, 575. Compds. contg. the *p*-nitrobenzoyl group are allylated and the allyl *p*-nitrobenzoate is reduced. E. g., *p*-nitrobenzoyl chloride is heated with allyl alc. at about 80°, or *p*-nitrobenzoic acid is esterified in the presence of HCl. The allyl *p*-nitrobenzoate thus obtained is a light yellow oil crystg. on cooling, m. 30° and  $b_D$  146–52°. Allyl *p*-aminobenzoate obtained by reduction of the latter compd. forms almost colorless needles, m. 54°. It is a local anesthetic. J. C. S.

Derivatives of cholic acid. J. D. RIEDEL. Ger. 334,553. Esters of cholic acid are treated with dehydrating agents. The products thus obtained are saponified and by subsequently acidifying the free acids are obtained. E. g., *methyl cholate* is heated with glycollic acid and  $KHSO_4$  at 130°. From the mixt. of unsatd. acids, *apocholic acid* is obtained as a compd. with  $AcOH$ ,  $C_{24}H_{38}O_4.CH_3CO_2H$ , forming needles, m. 150–60° (after sintering). After removal of the  $AcOH$ , the *apocholic acid* is almost tasteless. From the  $AcOH$  mother liquors, other unsatd. bile acids are pptd. by water; these are distinguished from *apocholic acid* by their greater soly. in ordinary org. solvents. Aq. solus. of the salts have a strong solvent action on many insol. substances. J. C. S.

## 18- ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The intensive manufacture of sulfuric acid. P. LEBRETON AND TRUCHOT. *Chimie et industrie* 9, 272(1923); cf. C. A. 16, 4015.—Controversial. A. P.-C.

The lead chamber process without chambers or towers. HUGO PETERSEN. *Chem.-Ztg.* 47, 227(1923).—In an ordinary Pb chamber plant, with intensive working, 200 tons Pb are necessary to produce 35 tons 50° acid per 24 hr. This Pb, without erection costs, constitutes about 40% of the total cost of the plant, exclusive of the roasters. Various efforts have hence been made to operate without either chambers or towers. P. in 1905 first pointed out how this could be done by using a 55° acid rich in N com-

pounds. (Cf. *C. A.* 1, 2293; 5, 3130.) The Opl tower system and the Schmiedel-Klencke system depend on this ability of 55° acid to be denitrated easily, or to take up N oxides readily. Various forms of app. to bring about the necessary intimate contact between the SO<sub>2</sub> gas and this acid were described by P. in his 1905 patent. Schmiedel and Klencke propose to bring this about by drums which revolve in the acid and spray it about. An extensive mechanical development hence replaces the chambers, costing more in upkeep and operation than is saved in interest and repairs by dispensing with the Pb chambers.

F. C. Z.

**Pyrite roasting and the manufacture of sulfuric acid.** CARL RITTER. *Chem. App.* 10, 25-7, 37-8(1923).—A brief discussion, with 10 cuts, of recent improvements in mech. roasters and Pb chambers.

J. H. MOORE

**Valentiner process for the manufacture of nitric acid.** WM. MASSON. *Mov. sci.* 13, 8-11(1923).—See *C. A.* 16, 615.

F. C. Z.

**Closure for acid carboys.** ANON. *Chem. Met. Eng.* 28, 534-6(1923).—A review of the report of the carboy test sub-committee of the Mfg. Chemists Assoc. A progress report and listing of 16 recommendations regarding general sealing, the stoppers, and stopper fastenings.

W. H. BOYNTON

**Production statistics of the alkali industry.** ANON. *Chem. Met. Eng.* 28, 593(1923).—Statistics compiled by the Census Bureau in the Dept. of Commerce for 1921 are given.

E. H.

**Synthetic ammonia by the Claude process.** ANON. *Mem. compt. rend. soc. ing. civils France, Bull.* April June 1922; *Chem. Met. Eng.* 28, 498-502(1923).—The use of 1,000 atm. calls for very careful selection of materials, which however can easily be obtained in sufficiently good quality. The safety factor is one of construction rather than of construction material. The difficulties in making joints tight are smaller for superpressures because of the smaller size of app. per wt. of NH<sub>3</sub> produced. The additional cost of producing superpressure is proportionally small, the work of compression increasing with the log. of the pressure. The efficiency of Claude's process is 4 times that of the Haber process, the amt. of catalyst, 0.1. This process does not require the costly heat-exchanging equipment of the Haber process. By cooling with water to ordinary temp. 97% of the NH<sub>3</sub> is liquefied. An iron catalyst at 300-400° converts the CO into CH<sub>4</sub> at the same time reducing all O to water. With gas thus purified the catalyst will last for 200 hr. The catalyst tube is so constructed that by the time the inlet gas reaches the catalyst it has attained the required temp. The substitution of tubes with new catalyst is done in much the same way as shells are loaded into heavy guns. H for the Claude process is purified by liquefaction. The cost of installation per ton of synthetic NH<sub>3</sub> by the superpressure process is less than half the cost for the Haber process. The relative simplicity of operation of Claude's process and the fact that it can be installed in small units are also to be taken into consideration.

HELGE SCHJESTED

**Report on the fixation and utilization of nitrogen.** Nitrate Div., Ordnance Office, War Dept., and Fixed Nitrogen Res. Lab., Dept. of Agr., No. 2041, 353 pp.(1922).—A comprehensive report which discusses the N situation of the world, with pertinent statistics. The history, chemistry, and construction and operating costs of the various processes are discussed, as well as a history and description of the U. S. Govt. nitrate plants. The report itself must be consulted for details.

F. C. Z.

**A new "wet" process of lime manufacture.** N. C. ROCKWOOD. *Rock Products* 24, No. 19, 25-8(1921).—An illustrated description of the patented process of Schaffer and Crow (cf. *C. A.* 15, 3191) for utilizing H<sub>2</sub>O vapor in calcination.

C. C. DAVIS

**Alsatian potash.** J. E. TEEPLE. *Ind. Eng. Chem.* 15, 419-20(1923).—After a visit it is concluded that the Alsatian K mines are efficiently run and capable of pro-

ducing 500,000 tons  $K_2O$  per year, thus insuring against a German monopoly.

F. C. Z.

**Niter cake.** H. H. GRAY. *Chemistry and Industry* 42, 225-6(1923).—A possible method of disposing of niter cake is to treat a soln. thereof with  $HCl$ , whereupon the reaction  $NaHSO_4 + HCl = NaCl + H_2SO_4$  occurs. In the lab. G. has obtained thus a 40%  $H_2SO_4$  soln. contg. less than 0.5% solid residue, when starting with a satd. soln.; and 60%  $H_2SO_4$  when starting with a satd. soln. in contact with solid niter cake.

F. C. Z.

**The manufacture of barium chloride.** GREGOR HARTMANN. *Chem. Weekblad* 20, 162(1923).—The manuf. on an industrial scale by reaction of  $HCl$  with  $BaCO_3$  is described.

R. BEUTNER

**The bromine industry in Germany.** M. DEBUSSY. *Chimie et industrie* 9, 245-58 (1923).—A description of the Kuhierschky and Kossuth processes of  $Br$  manuf., with an outline of the prepu. of the various org. and inorg.  $Br$  compds. which are of com. importance.

A. P.-C.

**Evaluation of decolorizing carbons.** M. T. SANDERS. *Chem. Met. Eng.* 28, 541-2 (1923).—The ultimate method for evaluating decolorizing carbons must take into account two factors. The various carbons do not act similarly on different solns. and the action of being an adsorption phenomenon follows the adsorption equation. The Hess-Ives tintphotometer depends upon the extinction coeff. for certain wave lengths of light, and gives good results. Special units for use with this instrument are tabulated.

W. H. BOYNTON

**The production of liquid oxygen for use on aircraft.** E. A. GRIFFITHS. *Trans. Faraday Soc.* 18, 224-39(1922).—A discussion on storage, transport and production of liquid  $O$ . A good glass vessel is nearly twice as efficient as a metal one, though the av. vessel used for household purposes is quite the reverse. The discussion includes absorbent material for removing residual gases, precautions necessary in exhausting the interspace, the rate of loss, sepn. of thermal leakage into its components, and methods of generating gas from the liquid at a definite and steady rate. Heylandt's and Griffith's vaporizers are illus. A lab. plant, a liquid  $O$  plant with expansion engine, and a portable Claude type  $O$  plant are described. The plant with expansion engine yields a liquid of 75% purity, and that of the portable Claude plant a liquid of 96% purity. W. H. B.

The modern trend in fertilizer plant operation ( $H_2SO_4$ ) (ARMSTRONG) 15.

JEEP, WILHELM: *Die Kitte und Klebstoffe*. 5th Ed. revised. Leipzig: B. F. Voigt. 147 pp.

KNOX, J.: *The Fixation of Atmospheric Nitrogen*. 2nd Ed. enlarged. London: Gurney & Jackson. 124 pp. Reviewed in *Expt. Sta. Record* 47, 320(1922).

KRÄTZER, HERMANN: *Wasserglas und Infusorienerde*. 3rd Ed. revised and enlarged by L. E. Andes. Vienna & Leipzig: A. Hartleben. 216 pp.

**Sulfuric anhydride.** P. AUDIANNE. U. S. 1,450,661, Apr. 3. An app. for making  $SO_2$  by the contact process comprises a chamber contg. vertical tubes around which the catalyst is placed. A mixt. of  $SO_2$  and  $O$  is passed up through the tubes and down through the catalyst while a substantially uniform temp. is maintained throughout the catalyst.

**Condensing apparatus for sulfuric acid.** HIDEOSUKE IYO and the KWANTO SANSO KABUSHIKI KAISHA. Japan. 40,526, Nov. 7, 1921. A condensing vessel for  $H_2SO_4$  in the cascade system is composed of a hemispherical acid-proof  $Fe$  vessel having a delivery orifice and a hemispherical porcelain or glass cover having an inlet orifice,

into which the delivery orifice of the preceding vessel is inserted and a hole at the top for discharging acid fumes. The connections are cemented with a mixt. of asbestos and gypsum.

**Apparatus for indicating the loss of sulfuric acid.** HIDEO UTSUNOMIYA and JUN-ICHI KAMIRYO. Japan. 40,620, Nov. 14, 1921. An automatic alarm is described to indicate loss of  $\text{H}_2\text{SO}_4$  in manufg. app., such as the Glover tower, tanks, etc. A Pb pipe attached to app. from which  $\text{H}_2\text{SO}_4$  is likely to leak delivers the leaking acid to an electrolytic cell contg. water and connected in circuit with a warning bell or lamp.

**Synthesis of ammonia.** GEORGE CLAUDE and the GOMEI KAISHA SUZUKI SHOTEN. Japan. 40,687, Nov. 17, 1921. The heat of reaction is used to heat the compressed reacting gases. The elevation of temp. in the app. is controlled by introducing only a part of compressed reacting gas through the heat exchanger into the catalyzer compartment, while the rest of the gas is introduced cold.

**Ammonia synthesis.** G. CLAUDE. U. S. 1,448,387, Mar. 13. See Can. 223,951 (C. A. 16, 4302).

**Powdered calcium carbonate.** JYOKICHI AOKI and SETSUJI NARAHARA. Japan. 40,442, Oct. 26, 1921. In a closed vessel dried and powdered  $\text{Ca}(\text{OH})_2$  is introduced and given a rotating motion. Hot  $\text{CO}_2$  is introduced and  $\text{CaCO}_3$  is deposited.  $\text{H}_2\text{O}$  evolved in the reaction is conducted into another chamber to react with  $\text{CaO}$ .

**Purification of gypsum.** SHOTARO FUKATA. Japan. 40,417, Oct. 25, 1921. Impure, waste or pptd. gypsum (1 part) is burned at  $128\text{--}190^\circ$  until the  $\text{H}_2\text{O}$  content becomes less than half a mol. for 1 mol. of gypsum and then powdered. About  $\frac{1}{10}$  part of  $\text{H}_2\text{SO}_4$  (65° Bé.) is dild. with 20-30 parts of  $\text{H}_2\text{O}$  and heated at about  $100^\circ$ ; the powdered gypsum is gradually added and agitated. Monoclinic crystals gradually develop. When the crystn. is completed, the product is scpd. from the acid, washed with  $\text{H}_2\text{O}$  and dried below  $60^\circ$ .

**Furnace for crystallization of sodium chloride.** TÔEMON KIRYÔ. Japan. 40,621, Nov. 14, 1921. Addn. to 37,758. Homogeneous heating of the crystn. pan is especially described diagrammatically.

**Apparatus for manufacturing sodium chloride.** SAKUTARO FUKI. Japan. 40,510, Nov. 4, 1921, Addn. to 38,854. Diagrammatical.

**Apparatus for slaking lime.** GUICHI SUGAYA. Japan. 40,525, Nov. 7, 1921. Diagrammatical.

**Zinc oxide.** J. A. SINGMASTER and F. G. BREYER. U. S. 1,450,704, Apr. 3. In carrying out the Witherill process with a working charge contg. high-grade Zn-bearing material low in gang, a porous distributing layer of slate coal or other substantially non-slugging material is interposed between the ignition fuel and the working charge to obtain  $\text{ZnO}$  nearly free from Pb.

**Apparatus for continuous burning of sulfur high in ash.** H. G. CHICKERING. U. S. 1,450,677, Apr. 3.

**Preparing diatomaceous earth and carbon for purifying liquids.** W. L. JORDAN. U. S. 1,448,846, Mar. 20. Diatomaceous earth which has been calcined at a temp. above  $980^\circ$  is granulated and impregnated with a carbonizable material, e. g., blood, tankage, glue, molasses or paper mill waste liquor, and the impregnated material is then heated to a charring temp. The product is adapted for purifying sugar solns.

**Decolorizing and absorbing carbon.** NAOKICHI SUZUKI. Japan. 40,529, Nov. 7, 1921. Dried tofu husks or powdered bean refuse, 100 parts, is immersed in a soln. contg. 50 parts  $\text{ZnSO}_4$  for 10-20 hrs. It is then mixed with powdered marble and  $\text{HCl}$  is gradually added until the evolution of  $\text{CO}_2$  has ceased. The mixt. is carbonized in an Fe tube. After cooling, it is boiled with dil.  $\text{H}_2\text{SO}_4$  to convert the sulfides into sulfates, filtered, washed with dil.  $\text{NaOH}$  and  $\text{H}_2\text{O}$ , and dried.

**Recarbonizing lime of crude calcined magnesite.** R. D. PIKE. U. S. 1,449,696, Mar. 27. Freshly calcined magnesite contg. CaO is passed directly to a rotary kiln where it is treated with flue gases from the calcining furnace at less than calcining temp. to effect recarbonation of the lime.

**Preserving cloth, paper, wood or other porous organic materials.** M. LANDAU. U. S. 1,448,276, Mar. 13. Fluosulfonates or  $\text{HSO}_3\text{F}$  is used as impregnating substances, together with tar oils, alc., acetone or other solvents.

**Detergent for glass and chinaware.** J. E. GROVER. U. S. 1,449,281, Mar. 20. A cleaning compn. is formed by boiling together  $\text{Na}_2\text{CO}_3$  2 lbs., borax 1 oz., S 1 oz., oil of citronella  $\frac{1}{4}$  oz., alum  $\frac{1}{2}$  oz., chlorinated lime 4 oz., glycerol 1 oz. and  $\text{H}_2\text{O}$   $\frac{1}{2}$  gal.

**Silicate dental cement.** H. WEYLAND. U. S. 1,450,467, Apr. 3. A cement adapted for filling teeth is formed of feldspar and MgO or other inorg. base and a soln. of a hydrolyzed org. Si compd., e. g., the product formed from dil. HCl and  $\text{Si}(\text{OCH}_3)_4$ .

**Fire-proofing agent.** TAIZAN SUGA. Japan. 40,506, Nov. 4, 1921. Borax 100 and boric acid 30 parts are dissolved into  $\text{H}_2\text{O}$  600 and mixed with  $\text{Al}_2(\text{SO}_4)_3$  in  $\text{H}_2\text{O}$  300. Al borate is thus produced and dissolved in boric acid. The agent is warmed to 70–80° for use.

**Photograph records.** J. P. ELLIOTT. U. S. 1,450,739, Apr. 3. A fibrous material such as long fiber mixed with asphalt is covered with a layer of thermoplastic record compn. and the materials are then heated and compressed together.

**Asbestos friction-clutch rings.** L. KIRSCHBRAUN. U. S. 1,450,319, Apr. 3. An unwoven felted asbestos facing is satd. with heated asphaltic base oil and is then baked until the impregnating material is substantially insol. in  $\text{CCl}_4$ . Cf. C. A. 17, 328.

## 19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

**American and English ball clays.** H. H. SORTWELL. *Bur. Standards Tech. Papers* 17, No. 227, 153–82(1923).—See C. A. 17, 190. C. H. K.

**Studies of the clays. II. Centesimal and rational analyses, use of microscope.** O. BOUDOUARD AND J. LEFRANC. *Bull. soc. chim.* 31, 1145–52(1922); cf. C. A. 17, 1117.—The rational analysis of Vogt depends on the facts (1) that clay, kaolin and mica are dissolved by boiling  $\text{H}_2\text{SO}_4$ , but quartz and feldspar are almost unattacked. (2) Boiling NaOH soln. (sp. gr. 1.8) attacks biotite but not muscovite. A centesimal analysis is made and an analysis of the portion extd. by boiling  $\text{H}_2\text{SO}_4$ . From these figures the kaolinite, muscovite, sand,  $\text{H}_2\text{O}$  and undetd. constituents are deduced. It is shown that the results of the rational analysis may be deduced from the centesimal analysis by ordinary methods of chem. calcul. Microscopic examn. greatly aids in the lithologic interpretation of the centesimal analysis. L. W. RIGGS

**Gilding glazed clay vessels.** P. P. BUDNIKOV. *Ber. Polyt. Iwanowo-Wosnessensk* 6, 211–20(1922).—B. has examd. various methods of gilding glazed clay ware. A suitable gilding soln. is produced by pptg. Au from soln. in aqua regia by hydrous  $\text{FeSO}_4$ . The ppt. is ground with 8–10% of a flux consisting of 6 pts. of basic Bi nitrate and 0.5 pt. of anhyd. borax, mixed with oxidized turpentine and lavender oil, and applied to the wares. A bright Au film is produced after baking at 650–900°. Paler hues are obtained if about 30% by wt. of  $\text{AgCl}$  is mixed with the gold. "Sulfur balsam" may likewise be employed for gilding. 100 g. of dry French turpentine is mixed with 20 g. of S and 20 g. of Venetian turpentine and boiled gently on an oil bath. Acids must be distd. off at intervals, and it is best to carry out the distn. in a stream of  $\text{CO}_2$ , a long glass tube being employed as a reflux condenser. To 8–9 pts. of the balsam so prepd.,

a soln. of  $\text{AuCl}_3$  contg. 1 pt. of Au, 4 pts. of concd.  $\text{HCl}$ , and 4 pts. of  $\text{HNO}_3$ , diluted with  $\text{H}_2\text{O}$ , is added, and the mixt. heated on an oil bath until the Au dissolves.  $\text{H}_2\text{O}$  is removed, and 7–8% of lavender oil and 12% of French turpentine are added, and the mixt. is heated until completely mixed. The resulting mass is dissolved in  $\text{CS}_2$  and filtered. The  $\text{CS}_2$  is evapd. off, and 5–8% of basic Bi nitrate added, and the resulting mass applied to the wares, which are then carefully baked at  $450\text{--}600^\circ$ . The reactions occurring have been investigated by studying the interaction of S and pinene.  $\text{C}_{10}\text{H}_{16}\text{S}$  or  $\text{C}_{10}\text{H}_{16}\text{S}_2$  is probably formed by reaction between pinene and S. With  $\text{AuCl}_3$ , the compd.  $\text{C}_{10}\text{H}_{16}\text{S}\cdot\text{AuCl}_3$  is probably formed, and by baking, this is probably decomposed into  $\text{C}_{10}\text{H}_{14}\text{Cl}_2$ , Au and  $\text{SCl}_2$ . Gold sulfide gives only a mat film, under the conditions of the expts. "Sulfur balsam" may be prepd. by the interaction, at room temp., of  $\text{S}\cdot\text{Cl}_2$  and turpentine, the evolution of  $\text{H}_2\text{S}$  and  $\text{HCl}$  being prevented by cooling. Used in conjunction with  $\text{AuCl}_3$  this gives even better films than the first-mentioned balsam.

J. S. C. I.

A few novelties in the chemical stoneware industry (KALTENBACH) 1. Furnaces adapted for heating glass (U. S. pats. 1,448,160–1–2–3) 9. Stationary horizontal furnace or oven adapted for heating glass (U. S. pat. 1,448,194) 9.

**Glass baking disb.** H. NEGRAUK. U. S. 1,450,330, Apr. 3. Yellowish transparent baking dishes of borosilicate glass are colored and rendered translucent by fusing mineral coloring matter, *e. g.*, chrome green oxide or Co oxide, into the glass near one surface.

**Two-part lenses.** H. R. MOULTON and E. D. TILLYER. U. S. 1,449,343, Mar. 20. The 2 parts of the lenses are heated together in a furnace charged with Na vapor in order to prevent vaporization of Na from the glass itself.

**Cobalt-chromium steel molds for glass.** R. D. SMITH. U. S. 1,449,789, Mar. 27. Mold parts for shaping glassware are formed of a steel contg. Cr 10–15 and Co 0.5–5%, which may also contain Mn 0.5, Si 4, Mo 1 and C 0.35–1.5%. This alloy lasts 20 times as long as chilled Fe.

**Leer conveyer for continuous sheet glass.** H. E. ALLEN. U. S. 1,450,571, Apr. 3.

**Apparatus for drawing sheet glass.** W. GRAY. U. S. 1,450,590, Apr. 3.

**Endless conveyer apparatus for drawing sheet glass.** W. GRAY. U. S. 1,449,038, Mar. 20.

**Gold coating mixture for glass or porcelain.** JIRO ISHIKAWA. Japan. 40,632, Nov. 14, 1921. Ten g. of Au is dissolved in aqua regia, 38.5 g. of "balsam sulfide" is added and the mixt. evapd. to dryness on a sand bath. The residue is washed with  $\text{H}_2\text{O}$ , and mixed with Al, U, and Bi resinsates and the whole is dissolved in a mixt. (A) of 200 g. of lavender oil, 100 g. rosemary oil, and 100 g.  $\text{PhNO}_2$ . "Balsam sulfide" is prepd. from 60 g. turpentine, 36 g. oil of turpentine, 16 g. flowers of S, 50 g. lavender oil, 10 g.  $\text{PhNO}_2$  and 20 g. rosemary oil. The 3 resinsates are prepd. from (1) K alun 50 g., resin soap 100, Al soap 10 and A 190; (2) U nitrate 50 g., resin soap 100 g., and A 150 g.; (3) Bi subnitrate 2.3 g., rosin 15.3 g. and lavender oil 32 g., resp.

**Deflocculating clay.** W. FELDENHEIMER and W. W. PLOWMAN. U. S. 1,447,973, Mar. 13. Clay is deflocculated by the action of an aq. soln. of resin in NaOH or Na silicate.

**Porcelain having the appearance of granite.** TOMOTARO KAWAMOTO and GOSUKE KATO. Japan. 40,582, Nov. 9, 1921. A mixt. of feldspar 50, silica 20, marble 20, clay 10, and limestone 5 parts is crushed, passed through a sieve having 15–20 mesh per 3 cm. and mixed with coarse granules of granite. The mixt. is molded under 40 lb. pressure and heated at  $1300^\circ$  for 10 hrs.

**Refractory material.** F. B. DANEGHOWER. U. S. 1,450,140, Mar. 27. Refractory



materials such as graphite and  $\text{SiC}_2$ , are bonded with a phenolic resin or condensation product which is carbonized by baking the material.

**Laminated highly refractory material.** M. F. BECHER and M. C. BOOZE. U. S. 1,448,684, Mar. 13. A highly refractory material not readily warped or cracked at high temps. is formed of successive layers of fireclay, ceramic-bonded  $\text{Al}_2\text{O}_3$ , and a combination of  $\text{MgO}$  and  $\text{ZrO}_2$ .

**Crystallizing alumina, beryllia or similar refractory materials.** E. THOMSON. U. S. 1,450,464, Apr. 3. The material to be crystd. is vaporized in a closed chamber and the temp. and pressure are maintained such that the vapor and solid phase are in substantial equil., while a solid object, e. g., a refractory grid, at slightly lower temp. is brought into contact with the vapor to effect a growth of crystals with sharp angles, smooth surface and substantially free from cavities.

**Artificial magnesia spinel.** F. J. TONE. U. S. 1,448,010, Mar. 13. A mixt. contg.  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  and a reducing agent such as coke is electrically smelted at a temp. sufficiently high to fuse the ores and reduce a portion of the metallic impurities to metallic form, the fused product is allowed to cool and the metallic impurities are sepd. to obtain an artificial spinel for use as a refractory.

**Aluminous abrasive.** T. B. ALLEN. U. S. 1,448,586, Mar. 13. An aluminous ore, e. g., calcined bauxite, is electrically smelted with  $\text{Al}$  (without  $\text{C}$ ) to form an abrasive which is free from detrimental carbides.

## 20—CEMENT AND OTHER BUILDING MATERIALS

J. C. WITT

**Behavior of hardened portland cement under pure water.** G. HAEGERMANN. *Zement* 11, 377-9, 388-90, 399-401, 412-3(1922); *Chimie et industrie* 9, 311(1923).—If the water is not changed, it first dissolves  $\text{CaO}$  from the cement, and when it is satd. there is no further change. If the water is changed, or with running water, it continually dissolves out fresh quantities of  $\text{CaO}$ . An impermeable and insol. coating must be applied to protect the cement, e. g.,  $\text{CaCO}_3$ , which explains why cement hardened in air or under natural water (contg. bicarbonates and free  $\text{CO}_2$ ) behaves better under water than one hardened under pure water. A. P.-C.

**Protection of cements against the action of acids.** C. R. PLATZMANN. *Zement* 11, 390-1(1922); *Chimie et industrie* 9, 312(1923).—P. investigated the use of "Margalite," a  $\text{PhOH}\cdot\text{CH}_2\text{O}$  condensation product prepd. by Marcussou. One kg. covers 2 m.<sup>2</sup> of concrete. Test pieces made from 1 part blast furnace slag, 0.25 part of trass, and 0.75 part of normal sand were treated with Margalite 3 weeks after prepn., and 10 days later were immersed in 10%  $\text{H}_2\text{SO}_4$  and 25%  $\text{HCl}$ , resp. After 33 and 47 days' immersion the crushing strength was 306-319 kg. per cm.<sup>2</sup>. A. P.-C.

**Crystalloids and colloids in the theory of cement.** M. VON GLASENAPP. *Zement* 11, 446-8(1922); *Chimie et industrie* 9, 312-3(1923).—Crystals of hydrated  $\text{Ca silicate}$  can be observed under the microscope. They are always in the form of needles, grouped in rosettes against a background which seems to be formed of very fine grains constituting a gel the opacity of which under the microscope increases with age. Even after one year this gel still retains its colloidal texture, and it is doubtless this constituent which plays the principal role in the hardening of the cement. The crystals of the rosettes can be reproduced and observed by applying a drop of water to cement dust under the microscope. A. P.-C.

**Effect of low temperatures on the hardening of cement.** H. KREUGER. *Beton u. Eisen* 21, 74-8(1922); *J. Soc. Chem. Ind.* 41, 635A.—K.'s investigations cover the effect of low temps. on the compressive strength of 1:3 cement and sand mortar contg. from

8% to 15%  $H_2O$ . The normal tests were for mixts. with 8%  $H_2O$ , and hammered into mold, 7 days, 345, and 28 days, 560 kg. per sq. cm. Immediate exposure for 3 days to  $-15^\circ$  to  $-18^\circ$ , followed by 1 day moist air at  $+15^\circ$  to  $+18^\circ$  and the rest in  $H_2O$  at same temp., showed reductions in compressive strength in cubes with 8%  $H_2O$  of only 23% and 16% for 7- and 28-day tests. Similar frost exposure tests beginning at the start, the middle and the end of the setting period showed the following reduction in compressive strength, resp.: for the 28-day test only 14%, 4% and 0%. Plastic mixts. made by hand contg. 12.7%  $H_2O$  showed normal tests, 7 days, 154 and 28 days, 317 kg. per sq. cm. The losses by immediate frost exposure were 30% and 35%, resp. The losses by frost exposure at beginning of set as above were, for the 28-day tests, 24.0%, 22.7%, and 17%, resp. Injury was avoided and normal strength developed if the mortars contg. 8%  $H_2O$  were kept for 2 days at  $+4^\circ$  to  $+6^\circ$  before the 3-day exposure to  $-18^\circ$ , followed by 1 day in moist air and the rest in water at  $+15^\circ$  to  $+18^\circ$ . Alternations of  $-18^\circ$  and  $+18^\circ$  on successive days, following 1 day of moist air at  $+15^\circ$  to  $+18^\circ$ , reduced the strength after 28 days by only 14%. If, however, the freshly mixed mortar was immediately exposed to  $-18^\circ$  for 1 day and then to 1 day in  $H_2O$  at  $+18^\circ$  and 1 day in air at  $-18^\circ$  to the end of test, the loss of strength in the 28-day test was 60%. Plastic mixts. (15%  $H_2O$ ) were weaker at the start and lost heavily by the alternating treatment. At  $+3^\circ$  the rate of hardening is only half of the normal rate at  $+15^\circ$  to  $+18^\circ$ . The practical point is that 2 days holding of the mortar at  $+4^\circ$  to  $+6^\circ$  protects it from damage by subsequent freezing. Reference is made to studies on cooling of fresh concrete in freezing weather by T. Yoshida, C. A. 16, 152.

JAS. O. HANDY

The hardening and the speed of solution of calcined gypsum. P. P. BUDNIKOV AND J. K. SYRKIN. *Z. anorg. allgem. Chem.* 125, 257-68 (1922).—A study of (1) the rate of soln. of gypsum calcined at temps. from  $100^\circ$  to  $800^\circ$ , (2) the role of the insol. form in retarding the hardening and (3) the peculiarities of the crystn. process. All samples were heated from 5 to 8 hrs., cooled rapidly, ground fine and 2 g. digested in a const. vol. of  $H_2O$  at  $20^\circ$ . A definite procedure was used since the soly. may vary up to 20%, depending upon the size of particle (cf. *Z. physikal. Chem.* 37, 385). Gypsum calcined at  $115-25^\circ$  was composed chiefly of  $CaSO_4 \cdot \frac{1}{2}H_2O$  and rapidly formed a strongly supersatd. soln., based on  $CaSO_4 \cdot 2H_2O$ . The soly. then decreased to a soln. only slightly supersatd. The existence of a soln. satd. with respect to  $CaSO_4 \cdot \frac{1}{2}H_2O$  could not be verified, indicating that the rate of crystn. of  $CaSO_4 \cdot 2H_2O$  was approx. the same as the rate of soln. of the hemihydrate, though the rate of crystn. exceeded that of the soln. of the hemihydrate, preventing the existence of a hemihydrate soln. Calcined at higher temps., soln. took place rapidly and then ceased, with no max. supersatn. or subsequent decrease in soly. as with calcination at  $120^\circ$ . A great difference was found between the products calcined at  $400^\circ$  and  $500^\circ$ . With the  $400^\circ$  product, supersatn. and hardening still took place, but with the  $500^\circ$  product, a normal satd.  $CaSO_4 \cdot 2H_2O$  soln. existed after 8 hrs. (cf. Glasenapp, *Studien über Stuckgips, tolgebrannten und Estrichgips*, Riga, 1909). If hardening were a result solely of the pptn. of dihydrate, dead-burnt gypsum would not harden, but since it does set slowly, a transformation of the insol. form of  $CaSO_4$  to the sol. form must occur. Though boiling ordinarily reduces the ability of gypsum to form supersatd. solns., it had the opposite effect on that calcined above  $400^\circ$ , the rate of transformation to sol.  $CaSO_4$  being accelerated. Calcined from  $500^\circ$  to  $800^\circ$ , gypsum showed a much retarded rate of soln. At first it dissolved rapidly until all the sol. form of anhydrous  $CaSO_4$  was in soln., after which the insol. form of anhydrous sulfate (the chief constituent) passed into soln. extremely slowly only after transformation to the sol. form. Dead-burnt gypsum contains considerable amts. of sol. anhydrous sulfate and its inability to harden is due to a phys. retardation by the

insol. form. A sharp transition temp. of calcination from hardening to non-hardening properties could not be detd., though with rise in temp. of calcination the soly. decreased progressively and hardening was retarded; this was probably due to increasing proportions of the insol. form of anhydrous  $\text{CaSO}_4$ .

C. C. DAVIS

**Alca cement.** H. S. SPACKMAN. *Concrete* (Mill Section) 22, 35-6(1923); cf. C. A. 16, 3374.—Alca (=Al + Ca) cement has been manufactured in Europe since 1912, from bauxite and limestone. Its av. chem. compn. is  $\text{CaO}$  35-45%,  $\text{Al}_2\text{O}_3$  35-45%,  $\text{Fe}_2\text{O}_3$  5-12%,  $\text{SiO}_2$  5-12%. The cement is now made at 3 French works and at 1 Swiss works. Each works sells the cement under its own trade name, such as "Ciment Electrique," "Ciment Fondu," etc. Alca cement attains a very high early strength, and evolves considerable heat while setting, which favors its use in cold weather. Alca cement could be manufactured in the U. S. from native raw materials but the cost would be higher than for port. cement. Economy in using the material tends to offset the high cost of production.

J. C. WIRT

**The mixing proportions of trass and lime.** H. BURCHARTZ. *Mill. Materialprüfung* 39, 240-50(1921).—Trass and lime were mixed by vol. in varying proportions. Tensile and compressive strengths were detd. for each mixt. at the end of 28- and 90-day periods. The most favorable mixt. of trass and lime was 1:1.5. The compressive strength reached a max. at these proportions. The tensile strength was greatest for a 1:1 mixt. The ratio of tensile strength to compressive strength is unusually low; for this no satisfactory explanation can be offered. A few expts. indicate that the addition of lime to a trass concrete lessens the tendency for the concrete to crack after hardening.

R. F. SCHNEIDER

**The laying of concrete by gravity.** H. JUSTE. *Arts & metiers* July 1922; *Rev. universelle mines* 16, 59.—The excess  $\text{H}_2\text{O}$  necessary in laying concrete by gravity decreases its strength, 8-10%  $\text{H}_2\text{O}$  decreasing the strength of a completely hydrated concrete 5-20%.

C. C. DAVIS

**Official transactions of the National Crushed Stone Association.** ANON. *Rock Products* 26, No. 5, 34-5(1923).—A symposium on the various phases of the crushed stone industry.

J. C. WIRT

**Transmission of sound by standard masonry partitions.** P. E. SAMIN. *Ind. Eng. Chem.* 15, 498-9(1923).

E. J. C.

**New specification for road tar (ANON) 21.** A new wet process of lime manufacture (Rockwood) 18.

DUMESNIL, P.: *Fabrication de la poussière blanche. Chaux. Ciment. Plâtre.* Paris: Revue des matériaux de construction et de travaux publics. 472 pp.

FRIISCH, J.: *Le plâtre. Fabrication. Propriétés. Applications.* Paris: Desforges. 246 pp. Fr. 12.

**White cement.** GIICHI YAMAZAKI. Japan. 40,565, Nov. 7, 1921. Eight parts of dolomite, composed of 19.4% sol. and 3.19% insol. silicic acids, 1.10%  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , 27.7%  $\text{CaO}$ , and 20.41%  $\text{MgO}$ , are crushed to about 1 cu. in., burned at  $800^\circ$  and mixed with 2 parts of feldspar, burned at  $100^\circ$ , the compn. of which is 74.50% silicic acid, 16.05%  $\text{Al}_2(\text{SO}_4)_3$ , trace of Fe, 2.25%  $\text{CaO}$ , trace of  $\text{MgO}$ , 4.65%  $\text{K}_2\text{O}$  and 1.85%  $\text{Na}_2\text{O}$ . The mixt. is powdered in a ball mill and sieved. The product is used instead of portland cement or by mixing with the latter and is specially suitable for use in sea water.

**White cement.** GIICHI YAMAZAKI. Japan. 40,566, Nov. 7, 1921. Eight parts of dolomite of the compn. given in the preceding abstract are crushed to 1 cu. in., burned

at 800° for a few hrs., and mixed with 2 parts of slag contg. 38.97% sol. silicic acid, 12.26%  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , 44.8%  $\text{CaO}$ , 2.32%  $\text{MgO}$ , and 1.64%  $\text{SO}_2$ . The mixt. is crushed in a ball mill and sieved. The product contains 25.62% sol. and 4.35% insol. silicic acids, 2.75%  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2(\text{SO}_4)_3$ , 38.30%  $\text{CaO}$ , 22.15%  $\text{MgO}$  and 0.48%  $\text{SO}_2$ ; it is especially used in sea water.

**Waterproof hardening agent of cement.** KOMAKICHI KATO. Japan. 40,368, Oct. 19, 1921. The agent is a mixt. of soy-bean protein 100 g.,  $\text{NaOH}$  50 g.,  $\text{Al}_2(\text{SO}_4)_3$  35 g., and  $\text{AcONa}$  30 g. It is used by painting its aq. soln. with a brush on materials manufd. from cement or by mixing with cement.  $\text{NaOH}$  may be replaced with a mixt. of  $\text{Na}_2\text{CO}_3$  and  $\text{Ca}(\text{OH})_2$ ;  $\text{Al}_2(\text{SO}_4)_3$  with alum, and  $\text{AcONa}$  with soap or  $\text{Ca}(\text{AcO})_2$ .

**Roofing.** W. H. Cady. U. S. 1,450,712, Apr. 3. Roofing sheets are covered with a mixt. of colored slate or similar granular material and a waterproof colored emulsion which may contain bituminous material, clay and  $\text{H}_2\text{O}$ .

**Roofing sheets.** T. ROBINSON. U. S. 1,449,058, Mar. 20. A coating of Cu or other suitable metal is electrodeposited on sheets of asbestos and cement compn. or other non-hygroscopic heat-resistant material.

**Asphalted composition shingles.** K. SCHUTTE. U. S. 1,448,155, Mar. 13. Shingles of asphalt-satd. felt are provided on one face with an asphalt coating and a granular facing and on the other face with a thin coalesced bituminous film of asphalt and clay.

**Impregnated wood shingles.** A. H. CARRIER. U. S. 1,448,614, Mar. 13. A woody material such as palmetto contg. long fibers and a pithy filling is freed from moisture *in vacuo* and then satd. with asphalt.

**Bituminous emulsion.** L. KIRSCHBRAUN. U. S. 1,450,685, Apr. 3. An emulsion which is non-coalescible on drying and is adapted for use on roads is prepd. from waste sulfite liquor, colloidal clay or other earthy colloidal material and a bitumen in dispersed phase.

**Rotary kettle kiln for drying and burning plaster stone, plaster and similar materials.** G. JOURNET. U. S. 1,449,326, Mar. 20.

**Wood preservative.** KISABURO OHMURA. Japan. 40,674, Nov. 17, 1921. A mixt. of naphtholsulfonic acid and 10% Turkey red oil is painted on wood. When the mixt. has penetrated into wood it is changed into insol. Na salt by applying 1%  $\text{NaOH}$  soln.

## 21—FUELS, GAS, TAR AND COKE

A. C. FRIEDNER

Some fundamental relations among the elements and compounds as regards the suppression of gaseous detonation. THOMAS MIDDLEY, JR. *Ind. Eng. Chem.* 15, 421-3(1923); *Chem. Met. Eng.* 28, 485-6.—The Nichols Medal address, including a portrait. C. C. DAVIS

**The use of waste fuels for producing electric energy in the mines of Dutch Limbourg.** A. S. TER LINDEN. *Ingenieur* Apr. 15, 1922; *Rev. universelle mines* 16, 228-31.—Extensive tests are reported using waste lignite and sludge. Detailed data are recorded with numerous diagrams for ordinary grates, chain-grates and mech. inclined grates. Lignite or lignite mixed with sludge can be burned on ordinary or inclined grates but not on chain-grates. By mixing lignite with sludge, clinker formation is reduced. Inclined grates cause least smoke, though thermally less efficient. Chain-grates are not suitable for sludge. C. C. DAVIS

**Dispersoid chemistry of peat. IV. Dehydration of peat at temperatures below 100°.** W. O. OSTWALD AND A. WOLF. *Kolloid Z.* 32, 137-8(1923); cf. *C. A.* 16, 4322.—Corrections of errors in preceding article (*C. A.* 17, 198). A. MUTSCHALLER

**Theory of fuel combustion in boiler furnaces.** W. E. GARNER. *Gas World* 78, 120-1 (1923).—Three zones may be distinguished in a fuel bed: an oxidizing zone, a reducing zone and a distn. zone. The thickness of the oxidizing zone is practically independent of the rate of supply of air to the fuel bed. The compn. of the gases leaving the surface of a fuel bed varies with the thickness; in general, the % of combustible gases rises as the thickness increases. One quarter of the combustible material is in the form of tar and soot. To burn the combustible gases secondary air must be admitted above the grate and in thin streams to secure rapid mixing. About 15-20% of the heat of the flame is emitted as radiation and this radiant heat is rapidly absorbed by the boiler surface. The rest of the heat is given up slowly by convection. A fuel bed of greater thickness than 4-6 in. is of no advantage, for at 4 in. above the grate the temp. is at a max. and the whole of the O of the primary air has been converted into CO<sub>2</sub> and a small % of CO. Combustion is incomplete in the case of thick fuel beds. Since an excess of air leads to a loss of heat in the flue gases, a negative pressure above the fuel bed should be avoided. With a natural draft alone, a negative pressure is unavoidable, and under these conditions, leaks of air into the furnace cannot be detected. Also, it is difficult to control the rate of combustion by natural draft on account of irregular changes in the thickness and resistance of the ash and coal. With forced draft changes in the pressure drop due to these causes may readily be compensated. The combustion chamber should be sufficiently large to allow for the combustion of all the smoke. The practical temp. attainable in the fuel bed is limited by the fusibility of the ash, which fuses in the reducing zone just above the zone of max. temp. J. L. WILEY

**Coal.** IX. KANSHI KURIHARA. *J. Chem. Ind. (Japan)* 25, 1327-47 (1922); cf. C. A. 17, 1703.—The hardness of coke prepd. from 175 types of Japanese coals, and of those on the market are given. The values are calcd. on the basis of kg. necessary to crush 1 cc. of the coke. The majority which are used for coke have a hardness of more than 45. The hardness of those cokes which are used by the steel industry in Japan run from 61.7 to 339.2. The hardness of foreign cokes are also given as a comparison. S. T.

**Some new derivatives of bituminous coal.** A. R. PEARSON. *J. Soc. Chem. Ind.* 42, 68-72T (1923).—The non-resinic constituents of coal often referred to as "cellulosic" or "humic" compds. are called "ultrahumins" in this paper. The portion of coal insol. in pyridine consists of  $\alpha$ -ultrahumins; the sol. but not resinic portion constitutes the  $\beta$ - or  $\gamma$ -ultrahumins. To prep. these substances the pyridine ext. of coal was concd. by distn. and poured into 10 vols. CHCl<sub>3</sub>. The colloidal ultrahumins were coagulated electrically, the  $\beta$ -ultrahumins collecting around the negative plate. These were filtered off and the pyridine filtrate with CHCl<sub>3</sub> washings was again concd. by distn. and then poured into an excess of ether which pptd. the  $\gamma$ -ultrahumins. The action of pyridine on coal is discussed from the colloid standpoint, this solvent being driven off by adding some ether which replaces the pyridine in the adsorption complexes. After the adsorbed pyridine in the  $\beta$ -ultrahumins was driven off by heating in a vacuum steam oven only 10% could be redispersed by boiling in pyridine, similar to an irreversible colloid such as hydrated silica, when heated. The  $\alpha$ -ultrahumins are not dispersible in pyridine but do hold considerable of it by adsorption. In the pyridinated condition the  $\beta$ -ultrahumins from all coals and the  $\alpha$ -ultrahumins from certain strongly coking coals gave firm cokes when carbonized, but after heating until most of the adsorbed pyridine was expelled the coking property was much reduced and in some cases entirely destroyed. The proximate constituents, computed on an ash-free basis, obtained from a South Yorkshire coal, were ultrahumins,  $\alpha$  85.8%,  $\beta$  7.2%,  $\gamma$  2.5%, resinic substances and loss (diff.) 4.5%. On treating these ultrahumins with concd. or fuming H<sub>2</sub>SO<sub>4</sub> each type gave colloidal oxidation products, "oxahumins." Analyses of these substances are

given and the C/H, C/N and C/O ratios are computed. The great stability of the N in the compds. is noted. The oxahumins as obtained in the dry state were hard, brittle, amorphous substances, black in mass, brown in fine powder. They formed deeply colored sols in H<sub>2</sub>O and to a slight extent in alc. and in pyridine. On bromination the oxahumins absorbed Br fairly rapidly up to about 1/3 of their wt. The product formed was pptd. with H ion, the ppt. when dried was a dark brown vitreous mass which was completely dispersed in both H<sub>2</sub>O and in alc. The alc. sol. was deep reddish brown in color, showed a strong Tyndall cone, and cataphoresis to the positive pole. The oxahumins and their Br products both form series of approx. const. compn. the analyses of which are given. P. concludes that the ultrahumins contain a very stable molecular nucleus of which N forms a part probably in heterocyclic combination. This stable nucleus is the same, or nearly so, for all the ultrahumins of the coal examd. but may be different for other bituminous coals. Even on brominating the oxahumins to satn. the oxidized nucleus or some portion of it still survives.

W. W. HODGE

**Nature of the organic matter extractable from coal by pyridine.** J. B. ROBERTSON. *J. S. African Chem. Inst.* 6, No. 1, 20-30(1923).—The coal studied was from Witbank, Transvaal; it contained C 72.06, H 4.01, N 1.72, S 1.03, ash 12.82, O (by difference) 8.36%. The C:H ratio is 17.97 and according to the classification of the U. S. Geol. Survey the coal would fall into the group "Bituminous F." This coal is similar to British coals in its behavior with pyridine and gives similar products on further treatment with CHCl<sub>3</sub>. The pyridine ext. was 15.4% of the wt. of the coal and 24% of this ext. was sol. in CHCl<sub>3</sub>. Alc. KOH exts. from the pyridine ext. substances which are of feebly acid nature, readily oxidizable, and form salts with aniline. Fused KOH oxidizes the pyridine ext. and causes a sepn. into an insol. portion low in O and a sol. portion relatively rich in O. Alk. permanganate oxidizes at least a portion of the pyridine ext. with the production of a solid material and phenols. No phenols are present in the ext. but they are obtained from it by decompn., heat or chem. reagents. It was not found possible to isolate any single constituent of the pyridine ext. to which a formula might be ascribed.

L. W. RIGGS

**The absorption of moisture by coal (and other fuels).** I. A relation between the degree of humidity in the air and the moisture content of coal. BURROWS MOORE AND F. S. SINNATT. *J. Chem. Soc.* 123, 275-9(1923).—When dried 200-mesh coal is exposed in a very shallow layer to room air, its wt. increases rapidly for about 24 hrs. and thereafter becomes a linear function of the humidity of the air, except for a very slow regular increase in wt. The wt. follows the humidity with little lag. Coals ranging from anthracite to peat were studied.

ERNEST W. TIMELE

**Electric furnace for the determination of coal-ash fusion temperatures.** OSBORN MONNETT AND J. F. KOHOUT. *Coal Age* 23, 329-30(1923).—Substantially the furnace consists of a 2-piece vertical refractory cylinder of Corundum with an inner cylinder of like material. Through these and at right angles to them passes a silica tube which serves as the muffle. Granulated C is the resistor material for a current not exceeding 35 amps. An atm. of gas from which illuminants have been washed is maintained in the muffle.

H. L. OLIN

**Recent installations and results in the practice of firing coal dust.** F. SCHULTE. *Glückauf* 59, 205-8, 240-7(1923).—An illustrated description of methods and equipment now in use in Germany, and the results obtained. Coal is recommended to be fired in the form of dust: (1) in firing small size and poor fuel, (2) when the grade of coal available continually varies, (3) with boilers with greatly fluctuating loads, (4) in large installations on account of the relatively low installation and operating expense per ton of ground fuel, (5) where labor saving is important and (6) in mining districts where dust is available without grinding.

C. C. DAVIS

**Brown coals and lignites.** W. A. BONE. *J. Roy. Soc. Arts* 71, 172-84, 189-99, 208-16(1923); cf. *C. A.* 16, 2019.—There is for each lignite a definite temp. limit (300-400°) up to which it may be heated in the dry state, so as to effect a considerable chem. condensation in its cellulosic or humic constituents, with simultaneous expulsion therefrom of steam and CO<sub>2</sub> and a small but variable proportion of CO; the chem. condensation is unaccompanied by any other change productive of either H or hydrocarbons; the consequent loss in wt. in the "dry ashless" coal substance may amount to 8-15% of its original wt.; such loss in wt. occurs at the expense of the O, which is reduced by 1/4 to 1/2 of its original value; practically the whole of the potential energy of the fuel is thus concd. in the residue, giving it a greater calorific intensity than the original coal when burned; such treatment thus constitutes a means of up-grading lignites, thereby improving their fuel values. *Briquetting* of lignites is discussed at some length. The best binder is pitch either from coal tar or from petroleum. Carbonizing tests at 375°, 500°, 700° and 850° with a dry brown coal contg. 30% O showed no evolution of any combustible gas up to 375° except a small amt. of CO. At 500°, CO<sub>2</sub> and water vapor appeared with small amts. of CH<sub>4</sub> and at this temp. about 1/3 of the available O was obtained as oxides of C and steam. Up to 700° the evolution of CO<sub>2</sub> fell off, but that of CH<sub>4</sub> rapidly increased; H also appeared; and 4/5 of the O came off as oxides of C and steam. Up to 850° there was a very large production of H. It is not to be expected that from lignites such high yields of tars and oils would be obtained as from bituminous coal. The low-temp. carbonization of these fuels would be largely from the point of view of improving the residual fuel. A promising field for these fuels is the direct burning of the pulverized, carbonized and raw form under boilers. By making use of the waste gases from the boilers for drying the fuel before it reaches the furnace, very satisfactory results have been obtained.

J. L. WILEY

**Examination of fatty tar oils.** J. MARCUSSEN. *Chem. Umschau* 30, 45-6(1923).—Fatty tar oils are the high-boiling portion of anthracene oil after the solid constituents are removed. The high viscosity of fatty tar oil, frequently increased by air blowing, makes it a good lubricating oil. The oil should be sol. in C<sub>6</sub>H<sub>6</sub>; any considerable residue indicates addition of coal tar or pitch. Permissible addition of lampblack, for purposes of better lubrication, is recognized by nitrating the residue with fuming HNO<sub>3</sub>; lampblack remains unattacked while tar forms nitro compds. sol. in acetone. Another portion is tested for soly. in acetone at room temp., in which it should be completely sol.; only air-blown fatty tar oils show a brown flocculation. A pitchy residue indicates addition of petroleum residues, which can be further identified by digesting 3 g. of the sample on the bath with 6 cc. of concd. H<sub>2</sub>SO<sub>4</sub> with stirring and pouring the product into 500 cc. H<sub>2</sub>O: a pure oil yields sol. sulfonic acids while petroleum residues give solid, black H<sub>2</sub>SO<sub>4</sub> addition products. Any addition of wood tar is recognized by dissolving the sample in ether and shaking it out with a 10% NaOH soln. which dissolves the hydroxy acids of the wood tars and can be sepd. by drawing off and acidifying the H<sub>2</sub>O layer. Mineral oils are identified by shaking 1 vol. of the sample with 1 1/2 vol. of Me<sub>2</sub>SO<sub>4</sub>, which dissolves the fatty tar oil, the insol. mineral oil rising to the top on standing.

P. ESCHER

**The utilization of palm oil as a motor fuel in the Gold Coast.** ANON. *Bull. Imp. Inst.* 20, 499-501(1922).—Tests were made using a 28-h.p. Tangye semi-Diesel, four-cycle engine. With palm oil contg. 5-6% free fatty acids which was not heated before placing in the supply tank, the engine started up from cold. After a continuous 24-hr. run there was no deposit on the cylinder walls and piston head, but a slight one on the atomizer and exhaust valve. The consumption was 0.24 lb. per h.p. hr. (0.20 lb. for mineral oil), and the amt. of cylinder oil required was reduced 75%. The engine ran far more regularly with palm oil and the exhaust gases were quite clear, showing

combustion was complete. No water injection was required with palm oil, which is attributed to its lower calorific value and to the presence of water in it. Its cost should be lower than that of mineral oil or not more than twice that of coal, in order to compete with them.

A. P.-C.

**Internal-combustion engine: its influence and its problems.** W. E. DALBY. *Roy. Inst. Gt. Britain*, May 26, 1922, 5 pp. (Separate).—Some remarks on the theory of combustion.

J. L. WILEY

**Determination of the calorific value of the volatile constituents of a coal as a measure of its suitability for the manufacture of gas.** R. MEZGER AND M. MÜLLER. *Gas u. Wasserfach* 65, 793-4(1922); cf. *C. A.* 15, 586.—Criticism has been made that the small amt. of coal (0.3 g.) used in the previous tests would not give accurate results. The app. was modified to use 3 g. of coal and the results were then found to agree closely with those obtained previously. Therefore unless large amts. of products are required, the previous and more convenient method should be used.

J. L. WILEY

**Gas requirements of, and composition of, exhaust gases from large gas engines.** D. RAUERT. *Stahl u. Eisen* 42, 1545-53(1922).—The efficiencies of two-stroke and four-stroke cycle gas engines are compared with reference to the loss of fuel in the exhaust gases. The importance of correct sampling of the exhaust gases so as to prevent any admixture with the external atm. sucked back into the exhaust tube, is emphasized. The loss of fuel in the exhaust gases with the two-stroke cycle is mainly due to inefficient scavenging of the cylinder. The percentage loss decreases with increasing load until the latter is about 75% of the full load, though the abs. loss remains approximately const. With the gas engines examd. the loss under a 75% load was about 10%, but this increased as the load was further increased until as much as 30% was lost when the engine was operating on a slight overload. The loss due to incomplete combustion during the working stroke decreases continuously as the load increases, varying from 30% at quarter load to 1 or 2% at full load. Only the latter loss is operative with four-stroke engines which are in consequence more efficient from this point of view.

J. S. C. I.

**The estimation of the moisture content of producer gas.** E. MAASE. *Feuerungstechnik* 11, 27-8(1922).—The app. consists of a water-jacketed container provided with a manometer and thermometer. The water jacket is heated, and a sample passed in. The inlet and outlet valves are closed, and the temp. is further raised to evap. entrained H<sub>2</sub>O. The thermometer and manometer are now read. Cold water (below the dew-point of the gas) is now run through the jacket, and the new temp. and pressure are detd. The H<sub>2</sub>O content may now be computed. The container is dried by passing in dry air.

ERNEST W. THIEL

**Thermal efficiencies of production of different grades of gas.** A. PARKER. *J. Soc. Chem. Ind.* 42, 111-17T(1923).—See *C. A.* 17, 1320.

E. J. C.

**Gas calorimetry.** T. A. CANNING. *Gas J.* 161, 694-6(1923).—The advantages and disadvantages of the Boys and Simmance-Abady calorimeters are stated and comparative results of tests on the Boys and Beasley instruments tabulated. Explanation is made of the methods of correction to be applied to the following sources of error to which the Boys instrument is liable: heat lost or gained in the exit gases; heat lost or gained by condensation or evapn. of water during the passage of air through the app.; radiation losses from the body of the calorimeter; errors due to assuming that 1 l. of water weighs 1 kg.; errors due to faulty calibration of the thermometers.

J. L. W.

**Combustion products from a radiant-type natural gas heater and suggestions regarding its operation.** GEO. W. JONES, W. P. YANT AND L. B. BERGER. *Bur. Mines, Repts. Investigations* No. 2443, 15 pp.(1923).—The radiant heater tested was a standard make with 10 radiants. The gas flow could be regulated either by a cock or adjustable orifice. With this type, CO is liberated only when the gas flow exceeds 15 ft.<sup>3</sup> per hr.,



(when the radiants glow more than  $\frac{3}{4}$  their entire length). The tests show that at a given gas flow, as the orifice pressure increases and likewise the air-gas ratio, the liberation of CO diminishes, and the efficiency of combustion increases. To obtain these conditions, the gascock should be opened wide, and then the orifice closed to give the desired gas flow or flame height. For a gas flow of 15 ft.<sup>3</sup> per hr. and the formation of no CO, the air-gas ratio should be 8 to 1. Directions are given for adjustment of the heater.

J. L. WILEY

Producer gas from powdered coal. R. T. HASLAM AND LOUIS HARRIS. *Ind. Eng. Chem.* 15, 355-7(1923).—Attempts have been made to make a satisfactory producer gas from powdered coal, but the process has not been extensively developed. The difficulties seem to be the production of a sufficiently high temp. in the reacting zone, and the maintenance of the necessary intimacy of mixing between the powdered coal and the reacting gas. In the expts. described, better results were obtained as the temp. of the incoming air was increased. It seems desirable to preheat the air for combustion to 1000° or over in order to reduce the time of contact or size of furnace required. The max. amt. of CO obtained in the expts. was 10.4%.

J. L. WILEY

Findings and report of the Therm Committee. C. G. HYDE, *et al.* *Gas World* 78, 238-42; *Gas J.* 161, 676-80(1923).—It is recommended that the method of charging for gas on the therm basis should be continued and extended to all statutory gas undertakings within the scope of the Gas Regulation Act.

J. L. WILEY

Some developments in gas producers. T. R. WOLLASTON. *Iron Coal Trades Rev.* 106, 196(1923).—Results obtained from gas producers of the recovery and non-recovery type are compared with those from an improved plant. Diagrams indicate the sources of loss and inefficiency as compared with the new plant; these are expressed in B. t. u. and money value. The R-G plant which furnished the data has a producer 9 ft. in diam. of 1300 lb. capacity per hr. The fuel is introduced through a retort in contact with hot exit gases and is thus partly coked, while the gases are enriched. The steam for the process is raised in an annular boiler around the unlined producer body. Blast satn. and superheat are derived from a central cone-shaped boiler within the producer which acts as a flash boiler. The precoking leads to a wide extension of the range of common fuels available, to practical elimination of clinkering, to great ease and economy of working, and to the production of a gas of unusually high value, CO<sub>2</sub> 10.6%, CO 18.8, H<sub>2</sub> 24.4, CH<sub>4</sub> 3.9, total combustible 45.1, heating value range 164.5 to 182.5 B. t. u.

J. L. WILEY

Experiences of vertical retorts at Stafford. JOSEPH POULSON. *Gas World* 78, 156-8; *Gas J.* 161, 528-31(1923).—During a 4-yr. period, many types of coal have been tried, and gas and by-product yield, rate of carbonization, throughput, fuel consumption, etc., are all found to be influenced by the physical properties of the coal. Easily carbonized coal means a great throughput, and results in fuel economy and thus lower mfg. costs. A dusty coal has the opposite effect through retardation of heat transmission. A better decompn. of steam takes place with an easily carbonized coal, because the coke is of open texture and of a friable nature and the size rather small and regular. Consequently, the gases have a longer time-contact with the coke, and at a higher temp., since the carbonization of the coal is completed earlier in its passage through the retort. With steaming to the extent of 21% with a steam pressure of 28 lb., 18,500 cu. ft. of gas are made of an av. calorific value of 437 B. t. u. There is available 7.75 cwt. of coke for sale after allowing for the fuel requirements. Many details of working are given. Waste-heat recovery is being practiced.

J. L. WILEY

Report of lignite-carbonizing experiments conducted at Grand Forks (N. Dak.) in 1922. W. W. ODELL. *Bur. Mines, Repts. Investigations* No. 2441, 26 pp.(1923).—Full details are given of the work outlined in C. A. 16, 1002. A lignite carbonizer was

devised and operated successfully for several months. By-products were not recovered but alterations are possible in the design of the carbonizer to allow it. The estd. cost and tentative layout of a plant of a definite capacity are given, and the costs of lignite-char and briquets are shown graphically. Lignite-char can be made at a much lower cost in this oven than in a by-product oven, hitherto suggested for carbonizing lignite. The oven described had a daily capacity of about 10 tons of raw lignite with a yield of char of about 45%. The efficiency of the process was as high as 65%. J. L. W.

**Steaming horizontal gas retorts.** G. W. BURKE AND C. J. MYERS. *Gas Age-Record* 51, 365-7(1923).—The steam was admitted at the rear of the retort for about 60 min. The results of the tests do not show any particular advantages either in an economical or practical way (cf. C. A. 16, 1006). The av. calorific values of the gas and the amts. of coke and breeze were about the same with or without steaming. With steaming an increase was observed in the  $\text{NH}_3$  production and a decrease in the amt. of gas and tar produced. The av. amt. of steam entering the retort was 178.7 lb. per ton of coal, of which 96.08 lb. were undecomposed. Steaming in the manner described is not profitable and is not to be recommended until a new and satisfactory method of introducing steam into the retorts has been devised. J. L. WILEY

**Retort vacuum and quality control.** W. H. WARREN. *Gas J.* 161, 619-22; *Gas World* 78, 183-5(1923).—The pressure in the retort should be kept at level gage during the entire carbonization in order to avoid leakage of gas from the retorts or of inerts into the gas. In connection with maintaining this level gage, the influence of correct design and functioning of the ascension pipes, dip-pipes, hydraulic main, foul mains and gages are discussed. J. L. WILEY

**Coal carbonization and the world's fuel.** H. C. PORTER. *Ind. Eng. Chem.* 15, 335-8(1923).—The increasing need for greater fuel economy is stressed. The possibilities of coal carbonization as a solution are discussed. Under present practice the cost of the process, due to high energy consumption and heavy plant expense, is prohibitive for general application. To develop carbonization processes either the expenditure of energy and the plant and operating costs per unit of output must be lowered or the "form value" of the products increased. In the latter direction low-temp. carbonization, particularly by its yields of oils, may make progress. Low-temp. carbonization in connection with complete gasification combines high heat economy and low operating costs with high "form values." For central plants the drawbacks are low B. t. u. gas and high delivery costs. J. J. MORGAN

**The use of active coal in the gas industry.** D. STAVORINUS. *Gas* 43, 64-9 (1923).—A review of modern methods for the absorbing of benzene and its homologs, of S and of tar, by means of charcoal. R. BEUTNER

**The extraction of benzene from gas.** J. RUTTEN. *Gas* 43, 111-2(1923).—By expts. and calcs. R. proves that the extn. of benzene pays only if a gas with too high a calorific value is produced which, for any reason, cannot be mixed with a poorer gas. R. BEUTNER

**Present state of the various processes for benzene recovery.** A. GREBEL. *J. usines gaz* 47, 1-9(1923).—G. discusses the known methods of benzene recovery under the headings: dissoln. or washing with heavy coal and petroleum oils, and with cresol and mixts. of hydrides of naphthalene (Brégeat process); adsorption or occlusion by active C (Voress, Bayer, etc.), and by silica gel, etc.; refrigeration (Bloch, DeVille); compression combined with washing (Claude), and with refrigeration. The work of Plenz, Bode and Werner (C. A. 17, 201, 461), Engelhart (C. A. 16, 4050), and Raschig (C. A. 17, 462) is reviewed. G. is in favor of the Brégeat process as being the most efficient. J. L. WILEY

**Removal of naphthalene from gas.** B. RICHARDSON. *Gas J.* 161, 384(1923).—

The most efficient and reliable method is absorption in a solvent, and the best app. is a mech. rotary washer-scrubber through which the gas and solvent travel counter-current. For efficient recovery prolonged and intimate contact must be effected between gas and solvent. For this reason bubbling the gas through an oil seal in a Livesey type of washer is impractical; the efficiency of removal is not greater than 56%. R. has found gas oil an efficient extractor, practically complete extns. being made at a cost of about 0.33 d. per 10,000 cu. ft. of gas. Also in *J. Soc. Chem. Ind.* **42**, 152-4T(1923).

J. L. WILEY

**Naphthalene determination.** OFFE. *Gas u. Wasserfach* **65**, 773-4(1922).—Mezger's method (*C. A.* **15**, 3201) for the detn. of  $C_{10}H_8$  in tar and tar oils can be shortened by using a U-tube in which the tar or oil is heated during the passage of a stream of H. The use of 100 cc. instead of 50 cc. of satd. picric acid soln. in the washer is recommended. The time required for the detn. is reduced from 3.5 to 2.25 hr. J. L. W.

**Burning blast-furnace gas.** GRANT D. BRADSHAW. *Blast Furnace and Steel Plant* **11**, 250-2(1923).—Types of burners for blast-furnace gas and for coke-oven gas are discussed.

E. H.

**Subjects and problems associated with distribution and utilization of gas.** F. L. OUGHTON. *Gas J.* **161**, 531-4(1923).

J. L. WILEY

**Oils and paints, etc., for gas-works preservation and maintenance.** H. CHALONER. *Gas J.* **161**, 460-1(1923).—Oil paints are the best protector against rust, but they cannot be used where high temps. may occur. A heat-resisting paint has a vehicle manufd. from gums and resins of a high melting point, so that when applied and subjected to heat it forms an impregnable film. The best base for it is a ferro-graphite. The best oil paint is one with a vehicle of boiled linseed oil and with the chief base of a ferro-graphite, which has a far greater resistance to corrosion, acids and alkalies than an ordinary red oxide of iron base.

J. L. WILEY

**What is the best quality of gas to declare, in the interests of seller and buyer?** J. F. TYNDALL. *Gas J.* **161**, 597-9(1923).—The best quality of all-round profitable gas to manuf. and supply to-day is a 500 B. t. u. mixed coal-gas and carburetted water-gas. However, local and individual circumstances must be the deciding factors.

J. L. WILEY

**New specific gravity apparatus for natural gas.** T. R. WEYMOUTH, R. P. ANDERSON AND J. R. FAY. *Ind. Eng. Chem.* **15**, 358-9(1923).—The app. comprises an orifice and a capillary tube in the same gas line with differential gages for each. The principle of its construction is based upon the measurement of the sp. gr. of a fluid flowing through a pipe line in terms of the differential pressure at the orifice. Directions for operating and calibrating the app., and its advantages as compared with the effusion app. are given.

J. L. WILEY

**Condensation losses due to transmission of carburetted water gas under high pressures.** W. A. DUNKLEY. *Bur. Mines, Repts. Investigations* No. 2447, 7 pp. (1923).—Losses due to condensation of the water vapor and condensible hydrocarbons are practically negligible in detg. the cause of unaccounted-for production. The decrease in gas vol. is negligible, and that in the heating value may amt. to 9 B. t. u. per ft.<sup>3</sup> or 1.6%. Pressures up to 75 lb. per in.<sup>2</sup> are considered.

J. L. WILEY

**Lighting and burners.** F. V. BARNES. *Gas World* **78**, 186-91; *Gas J.* **161**, 614-9(1923).

J. L. WILEY

**Development and progress in the production and refining of low-temperature tar.** ALFRED FABER. *Z. angew. Chem.* **36**, 1-3, 11-4(1923).—A resumé of the German low-temp. carbonization situation with tables and numerical data which cannot be adequately abstracted. It contains discussions of: English and American processes; characteristics of low-temp. tar, gas and semi-coke; German processes of low-temp.

carbonization in rotary kilns, generators and retorts (Pintsch) in connection with steam boilers; the recovery of paraffin wax, motor fuel, fuel oil and lubricating oil; processes for chemically changing the tar by cracking (Gräfe v. Walther, Strache-Stransky and Blümner), by hydrogenation without catalysis (Bergius) and by catalytic treatment with  $H_3PO_4$  (Melamid); the recovery, alteration and hydrogenation of the low-temp. phenols (Fischer<sup>3</sup> and hexalin processes). Many references to the German patent literature are given.

J. J. MORGAN

**Low-temperature coal tar and superheated products.** FRANZ FISCHER. *Ber.* 56, 601-3(1923).—A criticism of F. Schütz, *C. A.* 17, 1321. True low-temp. coal tar does not contain appreciable amts. of phenol or aromatic hydrocarbons. These products, as found by S., resulted from superheating of the tar during its prepn.

C. B. EDWARDS

**New specifications for road tar.** ANON. *Gas J.* 161, 448-9(1923).—The Ministry of Transport, England (Roads Dept.) have issued new specifications relating to the tar treatment of roads. General directions for applying are given. Tar as used must be coal tar except that the crude tar from which it is prepd. may contain not more than 15% of carburetted water-gas tar. No lower limit is placed on the sp. gr. or free C content of the tars than under the old regulations. Two types of tars are specified. Tar No. 1 is limited to 8% by wt. of naphthalene and No. 2 to 5% while the consistency of the former should be within the range 3 to 20 sec. and the latter within 20 to 100 sec., detd. by the Hutchinson tar-tester. When the consistency is between 15 and 25 sec., tars must not be supplied for either surface tarring or tar macadam unless specifically allowed by contract. Some special methods of testing for free C, naphthalene, and phenols are given.

J. L. WILEY

**Heating coke ovens with blue water gas.** "HAYDEN." *Gas World* 78, No. 2015 (Coking Sec.), 18-9(1923).—Directions are given for installing a blue water-gas system for heating a battery of coke ovens. The advantages of heating by an outside source of gas supply are given.

J. L. WILEY

**Possibilities of increasing ammonia yields in coke oven practice.** R. A. MOTT. *Gas World* 78, No. 2015 (Coking Section), 12-7(1923).—Increased yields of  $NH_3$  may be obtained in 2 ways: in decreasing the amt. of N left in the coke; in preserving the  $NH_3$  formed. The work of Monkhouse and Cobb in respect to the first point is reviewed (*C. A.* 16, 333, 2767), and that of Greenwood and Hodsman and of Hodsman and Mott for the second point (*C. A.* 16, 3744; 17, 1318). The possibilities and difficulties connected with the steaming of ovens are discussed. An increase in the yield of  $NH_3$  may be expected by steaming the charge during the last period of coking. Steaming is admissible, however, only if it does not affect deleteriously the quality and quantity of the coke, if it does not increase the coking time appreciably, and if it does not increase the amt. of inerts in the gas.

J. L. WILEY

**Determination of the specific heat of graphite and of coke within the temperature range 400 to 1300°.** E. TERRES AND A. SCHALLER. *Gas u. Wasserfach* 65, 761-4, 780-4, 800-2, 818-21, 832-3(1922).—In order to check up the work of former investigators (a review of which is given) on the sp. heat of graphite, and to establish the effect of various amts. of ash upon the sp. heat of coke, T. and S. have carried out a series of expts. on Acheson graphite and 2 coals made at 1000° and contg., resp., 15% and 30% of ash with almost identical chem. constitution. The app. and the exptl. methods are described in great detail. The weighed samples were heated to an accurately measured temp. in a weighed Pt dish in an elec. furnace, and then dropped into a receiver immersed in water in a calorimeter, the rise in temp. being noted. A detn. was made of the av. sp. heat of Pt for different temps.; the results compare well with those of former investigators. The results for graphite are very close to former

detns.; the sp. heat rises rapidly to 900° and then slowly and almost directly as the temp. The sp. heat of coke is made up of the sp. heats of the graphite and the ash, and is found to decrease as the ash content increases. The results of all detns. are shown in both tabular and graphic form. The sp. heat of the ash was compared with that of quartz, and a direct relation was found which permits the calcn. of the sp. heat of any coke with a known ash content from the values for graphite and for quartz. <sup>6</sup> J. E. WILEY

**Dry cooling of coke.** P. SCHLÄPFER. *Stahl u. Eisen* 42, 1269-75(1922).—The mean sp. heat of a coke contg. 10.5% of ash was found to be as follows for various temp. intervals: 18-100°, 0.214; 18-400°, 0.273; 18-477°, 0.286; 18-577°, 0.305; 18-800°, 0.333. In a dry cooling installation described, the coke is discharged from the oven into an enclosed chamber, and air is admitted. A small portion of the coke is thus burnt, until all the O of the air admitted has been utilized, after which the inert gases, consisting of N, CO<sub>2</sub>, and CO, are circulated through the cooling chambers until the temp. of the coke has fallen to about 250°. The sensible heat of the circulating gas is utilized for generating steam or for preheating boiler feed water. The speed of circulation can be regulated to suit the steam requirements of the plant. In one test, lasting 17 days, the wt. of coke cooled per day was 23.6 tons, and the water heated amounted to 9.4 tons, converted from water at 50° into steam at 94.5 lb. per sq. in. pressure (satd.), i. e., 0.398 kg. of steam per kg. of coke. Over a test period of 285 days, the steam generated amounted to 0.383 kg. per kg. of coke. J. S. C. I.

The Arca Regulator (SANDFORD) 1. Origin of coals (DONATH, LISSNER) 8.

GREENE, J. ARTHUR AND PERKIN, F. M.: "Patent," Smokeless and Semi-smokeless Fuels. London: Pitman. 127 pp.

SINNATT, F. S.: Inorganic Constituents of Coal. Pt. 3. The Chemical Composition of Iron Pyrites from Coal. London: Witherby.

WIRTH, FRITZ: Brennstoffchemie. Wissenschaftliche und praktische Grundlagen für Chemie und Technik der Verbrennungsvorgänge und der Brennstoffe. Berlin: C. Stille. 804 pp.

**Liquid fuel mixture.** M. LLOMPART Y VALDES and V. BACALLAO Y VILLAR. U. S. 1,448,245, Mar. 13. A fuel mixt. adapted for use in internal-combustion engines is formed of PhNO<sub>2</sub> 0.75, EtOH 99 and nitrous ether 0.25%.

**Fuel briquets from peat.** J. C. MORRISON. U. S. 1,450,107, Mar. 27. Peat of different grades is subjected to pressure and suction to remove H<sub>2</sub>O and is further dried by air or gas currents after being reduced to a loose bran-like condition. The portion contg. not over 25% H<sub>2</sub>O is carried off by the drying air or gas current, sep'd., mixed and briquetted and the briquets are superficially heated to incrust them with carbonaceous, tarry and oily substances.

**Coking coal.** S. R. ILLINGWORTH. U. S. 1,450,888, Apr. 3. See Brit. 186,384 (C. A. 17, 336).

**Vertical retort for coking coal.** W. WILD. U. S. 1,448,017, Mar. 13.

**Coal-carbonizing furnace.** H. L. DOHERTY. U. S. 1,449,591, Mar. 27. The furnace has an upright metal shell, of which only the middle portion is provided with a refractory lining. The upper end of the shell has a gas take-off and the lower portion has an inlet for air to support combustion.

**Apparatus for hydrogenating peat, lignite, sawdust, coal or other carbonaceous material.** T. ULKE. U. S. 1,449,875, Mar. 27. A horizontal inclined rotatable retort is provided with a double wall adapted to contain a temp.-regulating medium.

**Retort for destructive distillation of vegetable materials.** B. R. PFETTER. U. S.

1,449,544, Mar. 27. An app. for destructive distn. of straw or other vegetable materials is heated from beneath and is provided with a gas filter in its upper portion.

Apparatus for distillation of lignite. SHIGETARO YOSHIDA, TOSHIKA TANI and HUIZO YAMOTO. Japan. 40,392, Oct. 21, 1921. Structural features.

Treating gas from gas producers. O. PIETTS. U. S. 1,450,562, Apr. 3. Producer gas is passed into condensers and sprayed with  $H_2O$ , the temp. being adjusted by circulation of the  $H_2O$  so as to condense only fixed ammoniacal salts and tarry compds. The gas is then passed into a closed saturator in which the remaining ammoniacal compds. are converted into sulfate and the latter is crystd. Air blown under the grate of the gas producer is treated with the outlet water from the condensers.

Gas producer. E. H. WILSON. U. S. 1,450,767, Apr. 3.

Separating water from coal tar. P. JAWORSKI. U. S. 1,448,593, Mar. 13. A portion of a column of tar carrying entrained  $H_2O$  is heated sufficiently to reduce its sp. gr., but below the b. p., and permitted to impinge against a baffle to facilitate sepn.

Gas-valve for coke ovens. W. E. ROBERTS. U. S. 1,448,365, Mar. 13.

## 22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

The history and status of chemistry in petroleum research. C. O. JOHNS. *Ind. Eng. Chem.* 15, 446-9(1923).—An address. E. J. C.

Oil shale. V. C. ALDERSON. *Quart. Colo. School Mines* 18, No. 1, Suppl. B, 28 pp.(1923).—A resumé for 1922 with extensive bibliography. E. J. C.

Effects of temperature and time of reaction in distilling oil shales on the yields and properties of the crude oils. L. C. CARRICK. *Bur. Mines, Repts. Investigations* No. 2456, 8 pp.(1923).—Varying the rate of distn. of oils from oil shale changes the quality of the oil by modifying the temp. at which the decompn. takes place, and by influencing the extent to which the reactions of decompn. take place. The oils formed during slow distn. are formed at lower temps. than oils formed during rapid distn. Proper designs of commercial retorts should make possible the proper conditions of distn. so that oils of the desired quality can be produced. It is concluded, although the data are incomplete, that the % of S and N compds. in the crude oil decrease as the rate of distn. and the temp. maintained are decreased. W. F. FARAGHER

Petroleum oils obtained from castor oil and from shea butter. A. MAILHE. *J. usines gaz* 47, 66-8(1923).—Castor oil was treated over a catalyst of Al balls and Cu turnings at temps. from 540 to 570° and from 600 to 650°. At the former temp. a gas was obtained of compn.  $CO_2$  18%, CO 21,  $C_nH_{2n-36}$ ,  $C_nH_{2n+1}$  17.3,  $CH_4$  7.5, and liquid products which, after neutralization and hydrogenation and removal of the acids and the enanthaldehyde, form aliphatic hydrocarbons similar to Penn. oils. At the latter temp. a mixt. of aliphatic and aromatic hydrocarbons is formed similar to Borico oils. The acids sepd. from the hydrocarbons can be decomposed over the catalyst at 550° into gas and hydrocarbons, which by hydrogenation also furnish a petroleum spirit. The aldehyde also decomposes catalytically at 550° into gas and liquid. The latter is made up of light hydrocarbons such as  $C_4H_{14}$  and  $C_6H_{16}$ , the former has the compn.  $CO_2$  1.2%, CO 25.3,  $C_nH_{2n}$  40.8,  $C_nH_{2n+2}$  4.7,  $CH_4$  27.9. Castor oil then decomposes almost entirely into liquid and gaseous hydrocarbons, only a small amt. of the acids and the enanthaldehyde escapng decompn. Shea butter, between 630 and 650° and under the same catalytic treatment, is transformed into a mixt. of gasoline and kerosene contg. likewise some aliphatic and aromatic hydrocarbons, and into gas of a high calorific value and burning with a very luminous flame; its compn. is  $CO_2$  11.5%, CO 20.3,  $C_nH_{2n}$  43,  $C_nH_{2n+2}$  13,  $CH_4$  9, H 3. J. I. WILEY

Storage of fuel oil. FRANZ STANEK. *Chem. App.* 10, 31-2(1923); 2 cuts.  
J. H. MOORE

Theory of petroleum (MILSOM) 8. Apparatus for hydrogenating sawdust (U. S. pat. 1,449,875) 21. Tanning composition from acid oil sludge (U. S. pat. 1,448,278) 29. Oil filter (U. S. pat. 1,450,750) 1.

HÖFER-HEIMHALT, HANS: *Das Erdöl u. seine Verwandten*. 4th Ed. revised. Braunschweig: F. Vieweg & Sohn. 384 pp.

Selective oxidation of hydrocarbons. W. A. DARRAH. U. S. 1,448,655, Mar. 13. Fuel oil or a similar material to be partially oxidized is introduced into a rapidly moving current of heated gases contg. insufficient O for complete combustion, the pressure of the gases at the point of introduction being lower than at any other point of the system. A product thus obtained from fuel oil is adapted for use as a high-grade lamp black.

Petroleum from vegetable oils. KIYUHEI KOBAYASHI. Japan. 40,623, Nov. 14, 1921. Petroleum hydrocarbons are produced by heating a mixt of vegetable oils and Japanese acid clay at about 900°. The distd. oil has a greenish fluorescence, d. 0.818, sapon. value about 18.3, and contains about 9% fatty or petroleum acids, the yield being about 55% of the material. After treating with NaOH, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O as in the petroleum industry, it is fractionally distd. into 8.2% gasoline, d. 0.7382, 15.7% lamp oil, d. 0.8155 and 32.1% neutral oil, d. 0.8291.

Desulfurizing petroleum. P. VON DITMAR. U. S. 1,448,643, Mar. 13. The oil is heated with a metallic soap, e. g., an alkali or heavy metal soap, in a vessel from which liberated fatty acids can be drawn off and a small amt. of metallic Na is added during the reaction to prevent equil. checking the reaction.

Cracking petroleum oil. C. KROLL. U. S. 1,448,128, Mar. 13. A body of oil in a large horizontal cracking chamber is maintained under pressure and is heated to cracking temp. by hot combustion products passed through a horizontal flue extending through the chamber and surrounded by the oil. C deposits on the external surface of the flue are removed by a scraper.

Distilling petroleum oils. W. M. BURTON and E. M. CLARK. U. S. 1,448,254, Mar. 13. Liquid oil is heated to above its atm. b. p. under a pressure above 4 atm. to effect distn. and there is fed into the liquid from an external source a fresh stock of hydrocarbon having a b. p. under the prevailing pressure lower than the temp. of the liquid body, to superheat and crack the fresh stock added.

Distilling bituminous material. W. MEISCHKE-SMITH. U. S. 1,450,327, Apr. 3. Heavy Mexican crude oil, etc., which is to be distd. is fed into a combustion and distn. chamber together with balls of cast Fe or other incombustible material. Hot gases from a combustion zone pass between the incombustible balls and effect distn. and coking of the bituminous matter before reaching the combustion zone and after the balls have passed through the combustion zone they are removed and subsequently fed back for reuse.

Purifying mineral oil. J. SMITH. U. S. 1,450,617, Apr. 3. Oil is digested under pressure with absorbent cotton waste satd. with alkali by indirect steam heating with exclusion of air, to ext. P or S from the oil.

Pressure still and condensers for hydrocarbon oils. H. B. SETZLER. U. S. 1,449,452, Mar. 27. Heat is conserved by feeding oil to the still through the condenser.

Still for petroleum oils. U. F. CLEMENS. U. S. 1,449,734, Mar. 27. The still is of the horizontal type and discharges to a condenser through a pressure relief valve. A fuller's earth vapor filter is supported in the upper portion of the still.

**Digester and stirring apparatus for treating oils.** H. T. MAITLAND. U. S. 1,450,326, Apr. 3. The app. is especially adapted for recovering saponifiable oil from acid sludge obtained in lubricating oil refining.

**Apparatus for blowing air or other gases through molten asphalt.** H. R. WARDELL. U. S. 1,448,070, Mar. 13.

## 23—CELLULOSE AND PAPER

CARLETON E. CURRAN

**Chemistry of the sulfite process. IV. Distribution of sulfur during the cook.** R. N. MILLER AND W. H. SWANSON. *Paper Trade J.* 76, No. 10, 51-4(1923); cf. C. A. 17, 1328.—A study has been made of the distribution and state of combination of the S in a series of closely controlled sulfite cooks, total  $\text{SO}_2$ , total inorg.  $\text{SO}_2$ , combined  $\text{SO}_2$ , loosely combined  $\text{SO}_2$  and  $\text{SO}_3$  as sulfate being recorded for 8 cooks. The data given as to the location of the S do not point to any rule by which one can connect the formation of the org. S compds. or the exhaustion of the cooking liquor with the quality of pulp produced or the yield from the wood. The reactions involving the combination of hase and S with org. matter appear to be more or less independent of the reactions which govern the quality of the pulp. C. J. WEST

**Latex-casein top-sizing process.** F. KAYE. *India Rubber World* 68, 418(1923).—Whereas samples of paper which had been top-sized by means of on the av. 4.8% of their wt. of a mixt. of 75% rubber and 25% casein showed an av. increase in bursting strength of 26% (*India Rubber World* 68, 284; cf. C. A. 17, 341, 634). 11 samples of paper prepd. by the addn. of an av. of 0.77% of rubber in the form of latex in the beater showed an av. increase in bursting strength of 35%. G. S. WHITBY

**Report of the result of the investigation of five impregnation methods with regard to their action on paper yarn tissue.** G. HERZOG. *Mitt. Materialprüfungsamt* 39, 271-8(1921).—The investigation was carried out with both a heavy and a fine paper tissue. The methods consisted in treating the paper, which was cut in strips 20 cm. in width, (1) at 110-20° with a material which was solid at room temp. but fluid at temp. used, (2) at room temp. with a viscous fluid, (3) at 40° with the same fluid as used in the second method, (4) with a thin fluid at room temp., (5) with a thin fluid at 70-80°. After treatment the paper tissue was passed between rubber rolls, which removed any excess material. Various physical tests were made on the paper tissue previous to this treatment, and at intervals after it had dried. It was found in general that the strength had increased. The breaking point remained practically const. The fine paper tissue increased about 50% in wt. by the treatment, while the heavy tissue showed an av. increase of 70%. The paper tissue after treatment did not take up moisture to such an extent as the untreated tissue. Method 3 gave the best value for tensile strength with both kinds of paper tissue. Method 5 is of little value because the product is very slow in drying. C. T. WHITE

**Dyeing cellulose acetate** (U. S. pat. 1,448,432) 25.

**Cellulose ether compositions.** S. J. CARROLL. U. S. 1,450,714, Apr. 3. Perchloroethylene and MeOH or EtOH are used together as a solvent for cellulose ethyl ether in forming films, with the usual modifying ingredients. U. S. 1,450,715 specifies the use of Me salicylate and MeOH or EtOH in similar compns. U. S. 1,450,716 specifies furfural instead of Me salicylate. Cf. C. A. 17, 1329.

**Purifying cellulose ether.** P. C. SEEL. U. S. 1,448,091, Mar. 13. Cellulose ethyl ether is purified by treatment with 1-20%  $\text{HNO}_3$  followed by washing with  $\text{H}_2\text{O}$ .



Viscose threads or filaments. M. T. CALLIMACHI. U. S. 1,449,380, Mar. 27. A setting bath formed from potato starch, corn starch, etc., dissolved with  $\text{H}_2\text{SO}_4$  is used in forming threads or filaments from viscose. This soln. is stated to give better results than glucose in setting baths.

Frosting celluloid articles. SEIJIRO NAGAMINE. Japan. 40,366, Oct. 19, 1921. Articles of celluloid are frosted by immersing them in  $\text{MeOH}$ , dil.  $\text{AcOH}$ ,  $\text{Me}_2\text{CO}$  or exposing them to the vapor of the reagent, washing with  $\text{H}_2\text{O}$  and drying.

Paper from kapok fiber. A. LENDLE. U. S. 1,450,600, Apr. 3. Kapok fiber is used to form paper which is of a silky textile-like texture, adapted for covering boxes.

Safety paper. B. W. SMITH. U. S. 1,449,453, Mar. 27. A safety paper for negotiable instruments contains ultramarine and  $\text{PbCO}_3$  or other salt which will be acted upon by  $\text{H}_2\text{S}$  and a small amt. of  $\text{Na}_2\text{CO}_3$  or  $\text{CaCO}_3$  and is sized with Mn ferrocyanide soln.

Grease-proofing paper. W. L. WRIGHT. U. S. 1,449,718, Mar. 27. A flexible grease-proof coating on paper is formed from dissolved casein, a small amt. of  $\text{NH}_3$  and a vegetable oil, e. g., coconut oil, emulsified with  $\text{H}_2\text{O}$ . Cf. C. A. 16, 2780.

Sizing for paper. P. W. COOWISE. U. S. 1,449,892, Mar. 27. Hot  $\text{H}_2\text{O}$  contg. previously washed alum-tawed leather is treated with sufficient  $\text{Al}_2(\text{SO}_4)_3$  to bring the content of the latter *in toto* to 10% of the dry solids present, to form a sizing which is of light color.

Sizing for paper or cloth. R. KAISER. U. S. 1,448,847, Mar. 20. A dry sizing soln. in  $\text{H}_2\text{O}$  is formed of Karaya gum 98.5 and oxalic acid 1.5%.

Preheating apparatus for boiling liquid for paper materials. SEIJI KUWAHATA. Japan. 40,428, Oct. 25, 1921. Diagrammatical.

## 24—EXPLOSIVES AND EXPLOSIONS

CHARLES E. MUNROE

Seventieth birthday anniversary of Gustav Aufschläger, Feb. 9, 1923. A contribution to the history of the explosives industry. W. P. Z. *angew. Chem.* 36, 65-6 (1923).—In honor of this anniversary of Dr. G. A. M. Aufschläger, who joined the Muldenhütten dynamite works near Freiberg in 1882, became Gen. Director of the D.A.G. vormals Alfred Nobel & Co. in 1889 and has been an active factor in the explosives industry of Germany ever since, this issue of the *Zeitschrift* is an explosives no. and this article, besides consisting of a biographical sketch of A., with photograph, is an historical review of the Nobel Co. since its foundation at Hamburg in 1864.

CHARLES E. MUNROE

The nitroglycerin industry for upwards of a century. PH. NAUM. Z. *angew. Chem.* 36, 67-71 (1923).—A critical historical account of the manuf. of nitroglycerin from the discovery by Sobrero in 1847, and the first work of Alfred Nobel 15 yrs. later, to the present day describing methods of manuf., app. at different periods, changes in acid mixts., improvements in yields, introduction of L. F., polyglycerides and sugars, and recovery of spents. Except for Reese's application of  $\text{NaF}$  to the demulsifying of nitroglycerin emulsions no mention is made of any American work and even Reese's name is omitted. (Cf. C. A. 16, 4347.)

CHAS. E. MUNROE

Picryl sulfide. Study of the binary mixture: tolite-picryl sulfide. A. ROCHE and V. THOMAS. *Compt. rend.* 176, 586-9 (1923).—Picryl sulfide, used by the Germans as an explosive, m.  $211-34^\circ$ , and explodes at  $300^\circ$ . The binary mixt. with tolite has a eutectic at  $78.3^\circ$  and 86.5% of tolite. Mixts. rich in picryl sulfide can be readily supercooled.

T. S. CARSWELL

Memorandum on explosives for use in fiery and dusty mines and the methods of

testing, them. F. L. NATHAN. *Mines Dept. Safety in Mines Research Bd.* 12 pp., London, 1923.—A preliminary rept. of the recently established Explosives in Mines Research Comm. through its Chairman. It contains (I) an historical review of such researches from the "gallery" tests of Galloway, in 1875, to the establishment of the U. S. Bureau of Mines, (II) remarks on the gallery tests showing how very variable the conditions of testing are in the various countries, and (III) the program of the Comm. for further tests. A table giving the statistics for galleries in Belgium, France, Gt. Britain and U. S. emphasizes the marked differences between them, not only in dimensions, form and arrangement, but also in methods of procedure. C. E. M.

Liquid-oxygen explosives at Pachuca. M. H. KURYLEA AND G. H. CLEVINGER. *Mining & Metallurgy* 4, 149-52(1923); cf. *C. A.* 17, 881.—A detailed description of the methods pursued in obtaining the liquid O, and in making up, placing and firing the charges. The detonators are placed at the bottom of the bore hole and the LOX charges above them. No. 8 detonators fired by fuse are used. Trouble is at times experienced from "side-spitting" of the fuse. When fuse only is used LOX explodes like gunpowder. When detonators are used LOX detonates like dynamite. C. E. M.

Liquid oxygen in mining. ALFRED JAMES. *Bull. Inst. Mining & Met.* 1923, No. 222, 1-32.—Discussion of J.'s paper (*C. A.* 17, Apr. 20) opening with a fuller account of the technic, illustrated by cuts of plant and app. referring particularly to Harrington's Bur. of Mines Rept. on ventilation, recording an abnormal increase in temp. of the air of from 83.5° to 98° F. by explosion of 70 lbs. of dynamite in 14 holes in a 5X7 ft. crosscut; liquid O would have avoided that heat as well as the nausea and headache resulting from the CO generated. E. E. PALMER observed that as there is no flexibility to LOX cartridges the boreholes must be true to gage with a minimum 1/8 in. clearance. The necessity for this clearance provides for an air-cushion about the charge which must diminish its effectiveness. H. H. MORGANS pointed out that air-compressors as installed in Bolivia at 17,000 ft. elevation had about 1/2 the output capacity as at sea-level. H. F. MARRIOTT rehearsed many disadvantages of LOX, among them that the explosive cannot be concd. at the bottom of the hole for deep shots. A. James stated the fatal accidents from LOX in Lorraine occurred during tamping. CHARLES F. MUNROE

Application of the Devarda method to the determination of N in nitrocellulose (KOEHLER, *et al.*) 7. Determination of N in nitrates and nitrocellulose (KOEHLER, *et al.*) 7. Determination of N in nitroglycerin (KOEHLER, *et al.*) 7. Determination of NO (KOEHLER, MARQUEYROL) 7. Drying colloids (U. S. pat. 1,450,377) 13. Some fundamental relations among the elements and compounds as regards the suppression of gaseous detonation (MIDGLEY) 21.

Separating isomeric trinitrotoluenes. C. M. STINE. U. S. 1,450,875, Apr. 3. Crude mixed nitration products of toluene are treated with CCl<sub>4</sub> which effects sepn. of isomeric trinitrotoluenes.

Smoke-producing material. O. D. LUCAS. U. S. 1,448,073, Mar. 13. Pellets adapted for smoke production are formed of a pasty mixt. of KClO<sub>3</sub> and sugar (or flour) with auramine (for yellow smoke), "oil yellow" (for red) or purple or blue dyes.

## 25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

The synthesis of dicyanine. A. S. PALKIN. *Ind. Eng. Chem.* 15, 379-81(1923).—A new process is given for the synthesis of dicyanine A by the action of Na<sub>2</sub>S on alc. solns. of  $\alpha,\gamma$ -quinoline intermediates in the presence of small amts. of CHCl<sub>3</sub>. A yield

at least 12 times that of Mikeska, Haller and Adams (cf. *C. A.* **15**, 675) was obtained through a study of the influence of the solvent, concn. of OH ion, type of alkali, catalysts,  $H_2O$ , O, time and temp. on the reaction rate and on the relative yields of cyanine, di-cyanine, tar, etc.

C. C. DAVIS

The use of chromium compounds for mordanting and dyeing. *A. J. HALL. Am. Dyestuff Rept.* **12**, 189-92(1923).—Description of uses and applications of Cr compds. in dyeing of textiles, showing the influence on quality of dyeing. Methods of detection and estn. of Cr are given.

M. GRUNBAUM

The constituents of the benzene extract of American cotton. R. G. FARGHER AND M. E. PROBERT. *J. Textile Inst.* **14**, 49-65T(1923).—The authors treated Am. cotton in sliver form with redistd. 90% com.  $C_6H_6$ , heating with superheated steam. This made possible undesirable sapon. and, by condensation of steam, extn. of other materials. Crude ext. freed from  $H_2O$  and volatile hydrocarbons was successively extd. with light petroleum, ether, benzene, alc. and  $CHCl_3$  and divided into portions sparingly and readily sol. in a given solvent. The following substances have been identified: *Alcohols*.—The principal constituent is a new alc.,  $C_{28}H_{56}O$ , for which the name *gossypyl alcohol* (from *Gossypium spp.*) is proposed. *Montanyl alc.* ( $C_{28}H_{56}O$ ) is present in smaller amt. *Ceryl alc.* ( $C_{26}H_{52}O$ ), *carbauhyl alc.* ( $C_{24}H_{48}O$ ), a mixt. of phytosterols consisting chiefly of sitosterol ( $C_{27}H_{48}O$ ) and  $\alpha$ - and  $\beta$ -amyrin ( $C_{29}H_{48}O$ ) occur in small quantities. Sitosterol occurs also as the corresponding glucoside, sitosterolin. Little if any glycerol is present, as any glycerides present had been possibly sapond. during the extn. of crude material. *Acids*.—Palmitic, stearic and oleic acids occur in the free state; montanic, cerotic, palmitic and stearic acids and an acid,  $C_{28}H_{56}O$ , occur as salts, principally Na salts; carnaubic, palmitic, stearic, oleic and a lower isomeride of oleic acid occur as esters. The proportion of unsatd. acids free or combined is small. *Hydrocarbons*.—Cryst. triacontane and hentriacontane have been isolated. The greater portion of hydrocarbons present is liquid. *Gossypyl alc.* is not identical with melissyl alc. as seen from comparison of m. ps. of the alcs. and their derivs.; it appears to occur in 3 forms, different in m. p. and soly. in org. solvents, though giving identical derivs. and the same acid on fusion with potash-lime. It is proposed to term them at present:  $\alpha$ ,  $\beta$ , and  $\gamma$ . Variations are shown in the following table:

Form.	Solubility (g. per 100 cc.) in		
	Chloroform. (20°).	Ether. (25°).	Ethyl acetate. (25°).
$\alpha$ (m. 87-88°)	0.05	0.19	0.08
$\beta$ (m. 86°)	0.55	0.43	0.07
$\gamma$ (m. 82-83°)	0.64	1.09	0.09

The  $\alpha$ -form, the most insol., converted into acetate and regenerated into alc. by alk. hydrolysis, resembles closely the  $\beta$ -form. The  $\gamma$ -form, the form of greatest soly., appears in light petroleum ext., the  $\beta$ -form, of intermediate soly., in benzene ext., and the most insol. form,  $\alpha$ , in  $CHCl_3$  and alc. exts. *Montanyl alc.*, apparently not described before, is so named because its acid, produced by fusion with potash-lime, and derivs. appear to be identical with the montanic acid of montana wax, as shown by m. ps. *Gossypyl* and *montanyl alcs.* retain  $H_2O$  even when heated for several hours in vacuum at 115°. The anhyd. forms were obtained by sapon. of the acetates. Analyses of Schunck "cotton wax" (*Mem. Manchester Lit. Phil. Soc.* [3] **24**, 95(1871)) were found to be in agreement with the empirical formulas  $C_{28}H_{56}O$  for montanyl alc. and  $C_{28}H_{56}O$  for gossypyl alc. while the description agreed better with gossypyl alc. The tendency to retain  $H_2O$  necessitated a careful examn. of their derivs. *p*-Nitro- and *p*-bromobenzoates can be obtained in almost quant. yields. They crystallize well, and are well adapted for characterization. Liquid hydrocarbons and resinous material made it difficult to identify alcs. occurring as esters in the light petroleum ext. Small amts.

of gossypyl and montanyl alcs., sitosterol and amylin have been isolated after sapon. Of the acids, only carnaubic and the acid  $C_{31}H_{58}O_2$  need comment. Doubt is still expressed as to the existence of the former; it has therefore been studied, results verifying those of earlier workers. The latter is probably identical with an acid of the same compn. and m. p. isolated by Schalfée (*J. Russ. Phys. Chem. Soc.* 96, 325(1876)) who stated that melissic acid from beeswax was a mixt. from which an acid,  $C_{31}H_{58}O_2$ , could be isolated by repeated crystn. from ether and fractional pptn. of Pb salts. The corresponding *incarnatyl alc.* was isolated by Sundwik (*Zentr. Physiol. Chem.* 26, 58(1898)) from bumblebee wax, and by Rogerson (*C. A.* 4, 2291) from the flowers of *Trifolium incarnatum*.

M. GRUNBAUM

Investigation of the bleaching of cotton. P. HEERMANN AND H. FREDERKING. *Mitt. Materialprüfungsamt* 39, 254-67(1921).—Expts. were carried out with  $CaOCl_2$  to det. the effect of time of bleaching, concn. of bleach, and temp., on the strength, elongation, and wt. of the cotton. The time factor is of secondary importance. However, increasing the Cl concn. from 0.5 g. to 2 g. per l. caused a loss of 44% in strength, 30% in elongation, and 5% in wt. The above results were obtained from 50 bleaching periods of 75 min. at 20°. Increasing the bleaching temp. from 20° to 37° caused a decrease in strength of 45%, in elongation of 29%, and a loss in wt. of 9%. Concn. of bleach liquor = 0.5 g. Cl per l. Fifty bleachings of 75 min. each were made.

C. T. WHITE

Note on the bleaching of cotton with hypochlorous acid. R. L. TAYLOR. *J. Soc. Chem. Ind.* 42, 79-80T(1923).—Polemical. Cf. *C. A.* 17, 1152. If  $H_2BO_3$  is added in excess to a soln. of bleaching powder, it liberates  $HClO$  and neutralizes free lime, liberating Cl; this causes reversal of the reaction in the production of bleaching powder. Cotton and linen contain two kinds of coloring matter, A and B. A predominates in American cotton and very little is present in linen. This coloring matter is rapidly bleached by Cl and more slowly by  $HClO$ . B predominates in linen and is quite unaffected by either Cl or  $HClO$ . B is more readily attacked when either Cl or  $HClO$  and a hypochlorite are mixed.

W. H. BOYNTON

New research on fiber injury through washing and bleaching methods. P. HEERMANN. *Z. angew. Chem.* 36, 101-3, 106-11(1923); cf. *C. A.* 17, 885.—A review is given of the progress made in washing and bleaching methods. Cotton is more resistant to washing and bleaching agents than linen. Soap and soda, tetrapol and other agents contg. no available O cause less injury to the fiber than bleaching agents contg. available O. Agents of the latter class injure linen fibers to a considerably greater extent than cotton. Increasing the bleaching temp. from 20° to 28° causes a decrease of approx. 50% in fiber strength.

C. T. WHITE

Effect of metallic salts, of starch and of soap upon the tensile and ripping strain of cotton. J. HUENNER AND V. MALWIN. *J. Soc. Chem. Ind.* 42, 66-8T(1923).—Strips of high-class fabric made from sea-island cotton were impregnated with 1% solns. of various salts and the excess of liquid was removed by passing the strips through a mangle under uniform pressure. The tensile and the ripping strain were then tested before and after drying. A distinct weakening of both warp and weft was produced by  $CaCl_2$ , of the weft by  $ZnCl_2$  and of the warp after drying at 120° by boric acid. Borax after drying at 100° affects the warp more strongly than the weft.  $Na_2HPO_4$  slightly increases the tensile strain. Starch and soap slightly decrease the tensile strain. Salts have little effect on the ripping strain with the exceptions of  $Na_2SO_3$  and  $H_2BO_3$  by which the decrease is marked. Starch increases the ripping strain when air dried or dried at 100°, but when dried at 120° starch causes slight change. Soap increases the ripping strain to 30% above that of the original fabric. With satd. solns. of salts the reduction in both tensile and ripping strain was with few exceptions marked, although reduction

in ripping strain does not always accompany reduction in tensile strain. After washing out the salts the fabrics generally regained their strength. With  $\text{Na}_2\text{SnO}_3$  and  $\text{Na}_2\text{S}$  a tendering of the fibers takes place. The action of  $\text{ZnCl}_2$  is complicated as it mercerizes or parchmentizes the fibers.

L. W. RIGGS

The utilization of waste from wool washers. P. KOLB. *Chem. App.* 10, 30-1 (1923); 1 cut.—A few data on the cost of operation and profits in an Eng. plant.

J. H. MOORE

Bacterial retting. P. BETTINGER. *Bull. assoc. chim. suc. dist.* 39, 459-72 (1922).—B. shows the advantages of small agricultural distilleries undertaking the prepn. of textile fibers by bacterial retting and describes the various processes (Feuillette, Rossi, Kayser, Carbone), and more particularly the Kayser process.

A. P.-C.

Studies on the principal vegetable fibers in Japan. KIYOO ISHII. *Bol. Mag. Tokyo* 35, 127-37 (1921); *Japan. J. Botany* 1, 4A.—I. has examd. the chem. constituents and the dimensions of the following vegetable fibers in raw materials, and the results are as follows:

Samples.		Cellulose %.	Dimensions of the fibers. Length (mm.), Diam. ( $\mu$ ).	
<i>Corchorus capsularis</i>	Bast fibers	59.67	0.077-4.43	10-23
<i>Linum usitatissimum</i>	Bast fibers	66.70	10.2-50.9	13-31
<i>Boehmeria nivea</i>	Bast fibers	72.48	63-242	42-66
<i>Cannabis sativa</i>	Bast fibers	71.90	20.10-33.50	12-23
<i>Edgeworthia papyrifera</i>	Bast	46.45	1.20-5.14	14-32
<i>Wikstroemia sikokianum</i>	Bast	37.57	2.32-3.83	16-30
<i>Broussonetia Kasinoki</i>	Bast	56.00	0.94-21.07	12-42
<i>Morus alba</i>	Bast	46.74	1.25-25.41	10-32
<i>Oryza sativa</i>	Stem	38.31	0.29-1.41	5-29
<i>Avena sativa</i>	Stem	37.07	0.58-2.42	10-31
<i>Hordeum vulgare</i>	Stem	39.94	0.80-2.03	11-22
<i>Triticum vulgare</i>	Stem	42.11	0.46-2.01	11-22
<i>Phragmites communis</i>	Stem	46.23	0.51-2.33	8-22

E. J. C.

Sizing for cloth (U. S. pat. 1,448,847) 23.

ANDÉS, LOUIS EDGAR: *Wasch-, Bleich-, Blau-, Stärke- und Glanzmittel*. 2nd Ed. revised. Vienna & Leipzig: A. Hartleben.

BLAU, KARL: *Der praktische Kleiderfärber. Ein Lehr- u. Nachschlagebuch über d. gesamte Gebiet d. Kleiderfärberei*. Wittenberg (Bez. Halle): A. Ziemsen. 345 pp.

CLARKE, A.: *Coal-tar Colours in the Decorative Industries*. London: Constable & Co. Ltd. 166 pp.

JAUQUY, NICOLAS: *Die Entwicklung und volkswirtschaftliche Bedeutung der schweizerischen Teerfarbenindustrie*. Basel: Helbing & Lichtenhahn. 135 pp. Fr. 4.50.

ZÄNKER, WALDEMAR: *Die Färberei. Kurzer Lehrgang d. Färberei f. Textiltechniker*. 2nd Ed. revised. Leipzig: M. Jäneck. 269 pp.

Indigo dyeing of yarn. E. T. GARSED. U. S. 1,449,981, Mar. 27. Dye liquor is forced through yarn while wound on a beam and the yarn is then oxidized while being rebeamed.

Dyeing cellulose acetate. R. CLAVEL. U. S. 1,448,432, Mar. 13. Direct dyeing

of cellulose acetate in films, artificial silk or other forms is effected by an aq. soln. of a dye contg. not more than one sulfonic group and also contg. an active group in preponderating proportion over the sulfonic content of the mol., e. g. Galloxyaniline DH. Cf. C. A. 16, 4358.

*ar-α-Tetrahydronaphtholcarboxylic acid.* FARBENFABRIKEN VORM. F. BAYER & Co. Ger. 335,602. When dry CO<sub>2</sub> is passed over the dry Na salt of *ar-α-tetrahydronaphthol* for about one hr. at 110° and the temp. raised to 210°, *ar-α-tetrahydronaphtholcarboxylic acid* is obtained as a white, cryst. powder, crystg. in needles from glacial AcOH, m. 161–2°. The *acetyl* compd. crystallizes from 50% AcOH in needles, m. 159°. The *acid sodium salt* forms nacreous crystals. With diazotized nitroanilines and their derivs., for example, nitroaminophenolsulfonic acid, valuable azo dyes are obtained.

J. C. S.

**Sulfurized compounds of phenols.** A. THAUSS and A. GÜNTHER. U. S. 1,450,463, Apr. 3. By boiling phenols with caustic alkali and S, compds. are obtained which are generally yellowish powders serving as mordants for *fixing basic dyes* on cotton.

**Gas- and water-proof fabric for airships.** H. A. GARDNER. U. S. 1,449,748, Mar. 27. The fabric is impregnated with rubber and coated with a drying oil dope. The outer layer contains Al powder.

**Working up cotton.** SARURO KASUYA. Japan. 40,695, Nov. 18, 1901. Figures are printed on the cotton with a mixt. of 100 parts of H<sub>2</sub>O, 20 of starch and 5 of water glass; it is then immersed in concd. H<sub>2</sub>SO<sub>4</sub> (above 50° Bé.) for 5 sec. to 10 min., washed with H<sub>2</sub>O, and immersed in an alk. soln. of suitable concn. When the cloth is dyed after this treatment, shaded figures are developed.

**Wool cleaning.** H. Y. MCBRIDE. U. S. 1,449,613, Mar. 27. Wool is agitated with dead burnt gypsum. U. S. 1,449,826 relates to wool thus cleaned which is of open, "lofty," lustrous texture or natural color and with the scales or serrations of the fiber in their natural condition.

**Retting hemp, flax, perini or jute.** H. I. CROMER. U. S. 1,448,391, Mar. 13. The plant stalks are stacked in superposed layers in inclined position and after curing are subjected to the action of moisture while still in the stack but without submersion and are aerated after retting.

**Textile-scouring oil.** L. E. MURPHY. U. S. 1,449,240, Mar. 20. A liquid compn. of sulfonated castor oil and sulfonated maize oil is homogeneously combined with a neutral saponaceous detergent prepd. from olive-oil foots, lard oil, corn oil, coconut oil, neat's foot oil, caustic alkali and H<sub>2</sub>O.

**Apparatus for carbonizing woollen rags, combings, etc.** V. PIANA. U. S. 1,448,038, Mar. 13. The material is heated by combustion gases and treated with gaseous HCl.

**Spinning nozzle and associated devices for making artificial threads from congealed filaments.** B. BORZYKOWSKI. U. S. 1,450,131, Mar. 27.

## 26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

**Colloidal phenomena in paints.** CH. COFFIGNIER. *Bull. soc. chim.* 33, 128–32 (1923).—Exptl. evidence is given to support the theory that the premature thickening of paints having a resin varnish base is due to the formation of colloidal metal resinsates by reaction of the resin-free acid with a metal oxide. Coagulation in such paints is prevented by the neutralization or esterification of the free acid of the resin used in the varnish base. C. B. EDWARDS

**The determination of oil in oil paints.** HANS WOLFF. *Farben-Ztg.* 28, 930–1 (1923); cf. C. A. 17, 640.—The previously described rapid method for detn. of the amt.

of oil in a paint (*C. A.* 17, 640) is not applicable to paints contg. varnish vehicles. The results obtained are, however, influenced to a less extent than would ordinarily be supposed, by the presence of small quantities of resins. For accurate results, gravimetric methods must be used. In extg. with  $\text{Et}_2\text{O}$ , the rapid settling of the pigment is effected by addn. of 1 or 2 drops of  $\text{HCl}$ . If  $n$  of the isolated vehicle indicates the presence of resins, then a detn. of unsaponifiable matter, and of fatty oils and resin acids by the Wolff esterification method is necessary.

F. A. WERTZ

**Blue lead as a rust preventative.** ANON. *Gas-Age-Record* 51, 301-3, 314 (1923).—Sublimed blue lead is a basic sulfate of lead; it is obtained from the fumes produced in the smelting of galena ore. Tests made over a period of 6 yrs. in competition with various other pigments gave it a rating exceeded only by basic chromate of lead. It is a gray pigment passing through a 325-mesh screen. Its sp. gr. is 6.67. Sublimed blue lead in oil mixed with pure raw linseed oil and not more than 5% by wt. of drier will form a coating, the modulus of elasticity of which is far above that required by any deformation that can take place by expansion of the metal to which it is applied. One gal. of the mixt. will cover approx. 800 sq. ft. of surface. It is not affected by heat or cold within the range of normal atm. conditions nor is it affected by  $\text{S}$  and  $\text{CO}_2$  present in the atm.

J. L. WILEY

**Notes on the influence of colored and ultra-violet light on the drying time of linseed oil and varnish.** H. A. GARDNER AND H. C. PARKS. *Paint Manufs. Assoc. of U. S.*, *Circ. No. 172*, 148-51 (1923).—Films of raw linseed oil on glass plates were exposed in small inverted card board boxes. Holes were cut in the tops of the boxes, and then covered with colored and plain glass plates. After exposure to diffused light, the films under amber, blue, red, and ground glass covers were dry in 14 days or less; under green and plain glass covers, films were tacky but not dry in 14 days; and in a dark cabinet, the film was still as wet as originally. Exposure to direct sunlight caused the oil to dry in 2 or 3 days in all cases. Raw linseed oil contg. 0.2%  $\text{Co}$  dried in 6 hrs. under all colored glasses as well as in a dark box. Drying of raw linseed is greatly accelerated by an initial exposure for 0.5 hr. to ultra-violet light. The practical application of this accelerating effect is being experimented with in the varnishing of automobiles, etc. Cf. *C. A.* 13, 3023.

F. A. WERTZ

**The turpentine oil of the Crimea.** J. MAISSE. *Chem.-Ztg.* 47, 169-70 (1923).—Turpentine spirits from the Crimean black pine, *Pinus laricio pallastiana*, showed  $d_{20}^{20}$  0.864;  $(\alpha)_D^{20}$   $-24.92^\circ$ ;  $n_D^{20}$  1.4739. The results of fractional distn. of the spirits alone and over  $\text{Na}$  are tabulated. The oil consists principally of *l*- $\alpha$ -pinene; the low-boiling fraction contains small quantities of acetone. The rosin is optically inactive, m.  $71-73^\circ$ . Com. production of turpentine and rosin has been undertaken on a very small scale only.

F. A. WERTZ

**The identification constants of commercial linseed oils.** HANS WOLFF. *Chem.-Ztg.* 47, 142-5 (1923).—Analytical data on about 300 samples of commercial linseed oil, examd. over a period of years, are plotted. They show:  $d_4^{20}$ , limits 0.927-0.9310; 75% of total samples, 0.9285-0.9300; 88%, 0.9280-0.9305.  $n_D^{20}$ , limits 1.4788-1.4815; 85%, 1.4795-1.4810. I no., (Hübl, 16-18 hrs. at  $18-23^\circ$ ) limits 170-192; 77%, 172-177; 94%, 170-180. Sapon. no., limits 187-196; 87%, 188-192. Hexabromide no., 50-59, with a majority from 53 to 55%. The I no. on many samples was detd. also by the Wijs method (2 hrs.); the higher the I no., the greater the difference between the nos. detd. by the two methods as shown by the relation: Hübl no. = Wijs no. — (Wijs no. — 140)/5.

F. A. WERTZ

**The manufacture of varnish.** G. N. HILL. *Can. Chem. Met.* 7, 60-3 (1923).—A lecture; review.

F. A. WERTZ

**United States Government specification for asphalt varnish.** Federal Specifications

Board, standard specification No. 19. ANON. Bur. Standards, *Circ. No. 104*, 7 pp. (1923).—The varnish shall be composed of asphalt fluxed with properly treated drying oil, and thinned with a volatile solvent; shall be smooth and homogeneous, jet black in color; flash point (closed cup), 30° (min.); mix readily with linseed oil; insol. matter in  $\text{CS}_2$ , 1% (max.); non-volatile matter, 40% (min.); fatty matter, 20% of non-volatile (min.); rosin, absent; set to touch in 5 hrs., dry, hard and tough in 24 hrs.; film on metal must stand rapid bending over a 3 mm. rod; must withstand cold  $\text{H}_2\text{O}$  for 18 hrs., and lubricating oil for 6 hrs. When an acid-resistant varnish is specified, the film must withstand  $\text{H}_2\text{SO}_4$  (d. 1.25),  $\text{HNO}_3$  (d. 1.12), and  $\text{HCl}$  (d. 1.09) for 6 hrs. Details of the methods to be used in sampling and testing are given. F. A. WERTZ

Natural resins. FRITZ SIMON. *Chem.-Ztg.* 47, 141–2(1923).—A review, especially of the properties and detn. of the soly. of spirit-sol. copals. F. A. WERTZ

Nauli "gum;" a new oleoresin from the Solomon Islands. ANON. *Bull. Imp. Inst.* 20, 496(1922).—The tree from which was obtained a previously analyzed gum (*C. A.* 16, 2786) has been identified as *Canarium commune*, Linn. A. P.-C.

Poisoning symptoms from the solvents of airplane lacquers. H. W. VAN URK. *Pharm. Weekblad* 60, 293–6(1923).—The solvent contained in a lacquer known as "emanite" was found to consist of  $\text{C}_6\text{H}_6$ ,  $\text{MeOH}$ ,  $\text{AcH}$  and  $\text{AcMe}$ , the last 3 probably present as crude wood spirit. The characteristic poisoning symptoms of each of these constituents are enumerated and the inference is drawn that the mixt. would produce a summation effect. A. W. DOX

#### Oils and paints for gas works (CHALONER) 21.

Priming paint. RYUJIRO YANO and NAKAJIRO MANO. Japan. 40,496, Nov. 3, 1921. A soln. of  $\text{Ca}(\text{OH})_2$  3–4 and casein 10–15 in  $\text{H}_2\text{O}$  65 parts is added to a mixt. of sirupy tung or perilla oil 9–10, 5% borax soln. 1 and 10% alum soln. 1 and the whole is emulsified with a suitable quantity of pigment.

Paint. A. C. TUTT and L. F. SNELSON. U. S. 1,448,284, Mar. 13. A paint adapted for use on wood or metal is formed of a pigment contg.  $\text{Fe}_2\text{O}_3$  70,  $\text{ZnO}$  10 and  $\text{Cu}$  oxide 10 parts mixed with linseed oil 60 parts contg. a small amt. of rubber and amber.

Paint. J. T. LAWRENCE. U. S. 1,450,688, Apr. 3. A paint which is adapted for use on wood or metals is formed of oil 80,  $\text{BaSO}_4$  12,  $\text{Na}_2\text{CO}_3$  12, "prepd. white zinc" 24, white lead 12,  $\text{ZnSO}_4$  16,  $\text{SiO}_2$  12, ground white antimony 6, yellow rosin 6 and water white rosin 6 parts.

Paint for ship-bottom. SHINROKU SUMIDA. Japan. 40,421, Oct. 25, 1921. Three parts of  $\text{PhOH}$  contg. 10%  $\text{H}_2\text{O}$  are melted with 1 part of resin lac at 60–70°, and 4 parts of  $\text{Pb}_3\text{O}_4$  (or  $\text{PbO}$  etc.) are added. The paint thus produced is dild. with  $\text{C}_6\text{H}_6$  for use.

Antiseptic and anti-rusting paint. TAIZAN SHIGA. Japan. 40,388, Oct. 21, 1921. Adln. to 38,112 (*C. A.* 16, 1327). The paint is a mixt. of resin 1,000,  $\text{Cu}$  resinate 500, turpentine oil, benzene, naphtha or their mixt. 3,800,  $\text{CuO}$  400 and pigment (commonly  $\text{Fe}_2\text{O}_3$ ) 990 and 1,000 parts of a mixt. of linseed oil 800, tung oil 200 and litharge 100.

Solvent for paints or varnishes. MASAKUNI YANAGI. Japan. 40,665, Nov. 16, 1921. The solvent is a homogeneous mixt. of 4% soap, prepd. from vegetable fats or resins, 50% solvent naphtha, 10%  $\text{CHCl}_3$ , 20% acetone oil and 20%  $\text{KOH}$  in 14% alc.

Paint- and varnish-remover. I. A. FERRELL. U. S. 1,449,388, Mar. 27. Starch 24,  $\text{Na}_2\text{CO}_3$  3,  $\text{NaCl}$  6,  $\text{NaOH}$  7 oz. and  $\text{H}_2\text{O}$  4 gals.

Solvent for cellulose esters. H. F. WILLKIE. U. S. 1,449,156, Mar. 20. Solns. of cellulose nitrate or acetate adapted for use as coatings or varnishes are prepd. with



diethyl phthalate, EtOAc and a third liquid such as abs. alc.,  $C_2H_5$  or 95% alc. which forms a ternary or quaternary constant boiling mixt. with the diethyl phthalate and EtOAc.

**Pyroxylin enameling composition.** H. F. WILLKIE. U. S. 1,449,157, Mar. 20. A compn. adapted for enameling is formed of pyroxylin, EtOAc, alc. and a quantity of diethyl phthalate sufficient to gelatinize only a portion of the pyroxylin in a lower layer of a film formed from the compn. when applied and when the volatile constituents have evapd.

**Varnish.** P. ROTBERG and A. P. SACHS. U. S. 1,448,889, Mar. 20. An oil varnish free from cellulose ester and contg. triphenyl phosphate is prepd., in part at least, of gums such as kauri or manila gum which would be unsuited for use in ordinary oil varnish compns. but are rendered capable of use by the presence of the triphenyl phosphite, triphenyl phosphite, triphenyl horate or similar compds. which may be partially substituted for the gum.

**Coating for airplanes.** KOSHIRO SHISHIDO and KIROKU MATSUBARA. Japan. 40,472, Oct. 28, 1921. A heated mixt. of gelatin 100,  $H_2Cr_2O_4$  3.5 and  $H_2O$  500 is applied, then a mixt. of amyl acetate 100, celluloid 5, and bird-lime 3.5, and finally another coat of the first mixt.

**Ink for mimeograph.** FUKAKO YAMANOCHI. Japan. 40,608, Nov. 10, 1921. Ca soap is prepd. by heating a mixt. of newly prepd.  $Ca(OH)_2$  1, and animal or vegetable oil (except castor oil) 3 parts at about  $300^\circ$  with agitation. After cooling the soap is powdered and mixed with 12 parts of a mineral oil while heated below  $100^\circ$ ; to this product is added a mixt. of  $NH_4OH$  soln. of gluten 1 part, resin oil 3 and lamp black 1.

**Ink.** R. W. HILTON. U. S. 1,499,943, Mar. 27. A mimeograph ink is formed of a coloring material, e. g., carbon black or Prussian blue, mixed with an alk. salt of sulfonated oil, e. g., the  $NH_4$  salt of Turkey red oil, and trimethylene glycol.

**Ink.** W. O. SNELLING. U. S. 1,449,067, Mar. 20. An ink for writing is formed by suspending aniline black or other solid,  $H_2O$ -insol. particles (after reduction to sub-microscopic size) in  $H_2O$  with a protective colloid, e. g., gelatin or sol. starch products.

**Printing ink.** W. J. McELROY and J. CLARKE. U. S. 1,450,692, Apr. 3. A pigment such as a bronze powder is mixed with half its amt. of a soln. of coumarone resin 16% in 84% of a mixt. of terpineol 95 and rosin oil 5 parts.

## 27—FATS, FATTY OILS, WAXES AND SOAPS

E. SCHERER.

Annual review of the fat, oil and wax industry for 1921. W. HERBIG. *Z. deut. Öl-Fett Ind.* 42, 480-2, 494-5, 509-12, 526 30, 565-8, 581-3, 597-600, 631-5, 664-6, 677-81, 698-700, 713-5, 728-32, 746-9, 759-62, 776-9, 791-4, 807-9, 822-3(1922); 43, 3-6, 17-20, 36-8, 53-4, 67-9, 83-5, 100-2, 114 6, 131-2(1923).—A critical and detailed review with 772 references, under the following captions: A. Physical behavior. B. Chem. behavior. C. Analysis. D. Special analytical investigations. E. Individual vegetable fats and oils. F. Animal fats and waxes. G. Technical prepn. and utilization. G<sub>1</sub>. Refining of fats. G<sub>2</sub>. Splitting of fats. G<sub>3</sub>. Soap manif. G<sub>4</sub>. Special prepn. G<sub>5</sub>. Apparatus of the fat and oil industry. P. ESCHER.

Determination of the iodine number of fats, under unfavorable conditions. B. M. MARGOSCHES, RICHARD BARU and LISBETH WOLF. *Z. anal. Chem.* 62, 178-84 (1923).—The I no. of olive oil and soy bean oil was detd. by using the modified Aschman soln. and varying the conditions by omitting the solvent and agitation and varying the time. The I no. obtained with the use of solvent and agitation in 24 hrs. was 85.4 for olive oil. Without solvent but with agitation 85.1 was obtained in 24 hrs. With

solvent but no agitation 85.2 was obtained in 24 hrs., and without solvent or agitation 85.2. In the case of soy bean oil an I no. of 127.6 in 24 hrs. was obtained by the use of solvent, and agitation. Omitting the solvent but not the agitation gave 125.1 in 24 hrs. and omitting the agitation but not the solvent gave 122.7. Without solvent and without agitation a result of 108.8 was obtained in 24 hrs. E. SCHERUBEL.

**Refining, bleaching and deodorizing fatty oils and fish oils.** E. MYHRVANG. *Chem. Umschau* 30, 46-9, 56-8(1923); *Tecnisk Ukeblad* 1922, 354.—A general review.

P. ESCHER

**Cattle-bone fat and neat's foot oil.** H. ECKART. *Chem. Umschau* 30, 53-6(1923); cf. C. A. 16, 4082.—E. distinguished between edible fats obtained by boiling fresh bones, and inedible fats obtained by extg. old bones with solvents; in the former method the glue is lost, in the latter it is saved. Several tables of consts. of the oils and their fatty acids are reproduced. Cattle-bone fat and neat's foot oil contain, resp., stearic acid 19-21, 2-3; palmitic acid 20-21, 17-18; oleic acid 53-59, 74.5-6.5; glycerol 5-10, 5-10; unsaponifiable matter 0.5, 0.1-0.5%.

P. ESCHER

**Some West Coast vegetable oils.** ITTVERAH JOSEPH AND J. J. SUDBOROUGH. *J. Indian Inst. Sci.* 5, 133-56(1923).—The seeds of *Punna*, *Calophyllum wightianum*, from Travancore yield from 45 to 50% of a clear greenish yellow oil with a bitter taste. The consts. of the oil are:  $d_{15}^{20}$  0.939;  $n_D^{40}$  1.4733; solidifying point  $-5^\circ$  to  $-8^\circ$ ; acid value 18; sapon. no. 187; I no. 102; Hehner no. 92.3; unsaponifiable matter 1.8%; titer test 21.0°; mean mol. wt. 297. The refined oil is free from the bitter taste. *Maroti* oil is extd. from the seeds of *Hydnocarpus wightiana* to the extent of 41%. Its consts. are:  $d_{25}^{20}$  0.956;  $n_D^{40}$  1.4742; solidifying point  $17.8^\circ$ ; acid value 8.7; sapon. no. 199; I no. 96.5; unsaponifiable matter 0.42%; titer test 42.10; Hehner no. 95.5; neutralization no. 206; mean mol. wt. of fatty acids 273. The oil is very hard to refine. The main constituents of the insol. fatty acids are ebaulmoogric and hydnocarpic acids, which, according to Walker and Sweeney, have 100 times the bactericidal effect of phenol. The *cashew tree*, *Anacardium occidentale*, yields an oil from the nut kernel and from the husk. The former is edible but of no com. importance. The husk oil contains anacardic acid,  $C_{22}H_{32}O_8$ , a phenolic compd. cardol,  $C_{22}H_{32}O_8$ , and a substance sol. in ether. It is used as a disinfectant for wood and medicinally. The husk contains 39.8% oil with  $d_{15}^{20}$  1.0131; acid value 107; sapon. no. 119; I no. 296;  $n_D^{41.5}$  1.5158. E. SCHERUBEL.

**The colorimetry of fatty oils.** H. HELLER. *Farben-Ztg.* 28, 857-8(1923).—A review of the usual methods of designating the colors of liquids, with a preliminary suggestion on the use of a color comparator which promises to measure the colors of liquids by referring them to the Ostwald color circle. Cf. C. A. 17, 1343. F. A. W.

**Tentative standard test methods and percentages of oil and moisture in hair press cloths.** F. R. MCGOWAN AND C. W. SCHOFFSTALL. *Bur. Standards, Tech. Papers* No. 231, 257-76(1923).—Hair press cloth is used in the oil-pressing industries on account of the resiliency of the fibers; and since the fabric is bought on a wt. basis, the  $H_2O$  and oil which are added to permit efficient manuf. become important items. The petroleum ether extn. method is used to obtain the oil content. The standard % obtained by testing 27 samples are as follows:  $H_2O$  11%; oil 5%;  $H_2O$ -sol. material 2.5%.

E. SCHERUBEL

**A new oil seed from the Gold Coast.** ANON. *Bull. Imp. Inst.* 20, 463-5(1922).—*Kisidwe* nuts (*Allanblackia* sp., probably *A. floribunda* (Nat. Ord. Guttiferae) consist of shell 38.4%, kernel 61.6%. The latter contained 1.9%  $H_2O$ , and on extn. with light petroleum ether yielded 71.8% (72.3% on dry basis, and 44.2% on nuts as received) of hard white fat with a faint odor, which showed:  $d_{15}^{20}$  0.8563,  $n_D^{40}$  1.458, m. (open-tube method)  $38.6^\circ$ , solidifying point of fatty acids  $57.6^\circ$ , acid value 1.0; sapon. value 190.8, I value 44.2%, unsapon. matter 0.4%, volatile acids (cc. 0.1 N alkali required

to neutralize acids from 5 g. of oil) sol. 0.11, insol. 0.10. These consts. agree with those recorded for the fat of *A. stuhlmannii*, Engl. The residual meal contained (caled. to 7% fat): H<sub>2</sub>O 9.3, crude proteins 16.4, fat 7.0, carbohydrates (by difference) 52.2, crude fiber 8.9, ash 6.2%, nutrient ratio 1:4.2, food units 111. It contained no alkaloids or cyanogenetic glucosides, but a small amt. of tannin was present. A. P.-C.

**Chemical composition of the nut, *Irvingia Smithii*.** J. PIERAERTS. *Bull. agr. Congo Belge* 13, 460-4(1922).—A chem. study has been made of the *Irvingia Smithii*. The fruit studied consists of 84.75% hull and 15.25% kernel. The hulls make good fuel leaving a total ash of 0.55%. The kernel has 2.88% ash of which 0.96% is sol. in H<sub>2</sub>O. The total N content is 1.26, fat 75.03, P<sub>2</sub>O<sub>5</sub> 0.34. A complete analysis of the fat extd. in petroleum ether is given as well as the fatty acids from the materials. The fat is similar in properties to coconut oil. M. S. ANDERSON

**A rapid method for the determination of acidity in palm oil.** A. STRELTJES. *Bull. agr. Congo Belge* 13, 232-4(1922).—An alc. soln. of the oil is titrated with 0.5 N NaOH, with phenolphthalein indicator. Calcu. of acidity is made assuming only oleic acid to be present. M. S. ANDERSON

**Oil-producing nuts (*Irvingia*).** J. PIERAERTS. *Bull. agr. Congo Belge* 13, 68-82 (1922).—Chem. studies are reported giving the compn. and phys. consts. of oil from several species of nuts, particularly of the *Irvingia*. M. S. ANDERSON

**Utilization of lime seeds.** ANON. *Bull. Imp. Inst.* 20, 465-8(1922).—Clean dry lime seeds were crushed, heated to 120° F. and pressed. The filtered oil (30% yield) had the following consts. as detd. at the Imp. Inst. and at the Leeward Islands Lab., resp.:  $d_{4}^{20}$  0.9236,  $d_{15.5}^{20}$  0.9138;  $n_D^{20}$  1.4635,  $n_D^{25}$  1.4740; solidifying point of fatty acids 34.0°, —; acid value 13.6, 11.2; sapon. value 197.7, 193.6; I value (Hübl, 17 hrs.) 109.5, 100.75%; unsapon. matter 0.4, 0.72%; volatile acids (cc. 0.1 N KOH required to neutralize acids from 5 g. of oil) sol. 0.27, —; insol. 0.48, —. Refining with alc. or NaOH removed the bitter taste, but the refined oil did not possess the bland taste required for edible oils. The crude oil would be suitable for soap manuf. and could be used in admixt. with linseed oil for certain industrial purposes; but it would not be suitable for refining. The oil-pressed residue (30% oil removed) and crushed seeds contained, resp.: N 4.9, 3.43; K<sub>2</sub>O 0.685, 0.48; and P<sub>2</sub>O<sub>5</sub> 1.05, 0.74%. For feeding purposes the meal and crushed seed contained, resp.: H<sub>2</sub>O 15.08, 10.54; crude proteins 30.50, 21.37; true proteins 20.70, 14.50; fat 14.20, 39.87; carbohydrates 17.00, 11.90; crude fiber 20.05, 14.10; ash 3.17, 2.22%. The meal compares favorably in feeding value with undecorticated cotton-seed meal. A. P.-C.

**Losses in the refining of edible oils.** B. H. THURMAN. *Ind. Eng. Chem.* 15, 395-7(1923).—This article discusses losses caused by H<sub>2</sub>BO<sub>3</sub> and NaOH pptns., also refining, bleaching, hydrogenation and deodorization losses. E. SCHERUBEL

**The analytical detection of rancidity.** R. H. KERR AND D. G. SORBER. *Ind. Eng. Chem.* 15, 383-5(1923).—The first analytical indication of rancidity is the presence of labile O. The test of Vintilesco and Popesco is used to detect this (procedure described). E. SCHERUBEL

**Sulfuric acid test for fish liver oils.** NORMAN EYERS AND H. J. FOSTER. *Analyst* 48, 58-60(1923).—The production of a violet color on the addn. of a drop of H<sub>2</sub>SO<sub>4</sub> to a drop of the oil is not confined to fish liver oils but is given by other oils rich in vitamin A, such as butter fat. The sensitiveness of the test is greatly increased by adding an oil which itself gives no color with H<sub>2</sub>SO<sub>4</sub>. The min. amt. of cod-liver oil which gives the test is 0.04 cc. but by adding 0.1% cc. of olive oil, 0.01 cc. of cod-liver oil will give the color. The test is carried out as follows: The oil or a soln. of the oil in petroleum ether, purified by shaking with concd. H<sub>2</sub>SO<sub>4</sub> and sepd., is measured into a test-tube; 2 drops of olive oil are added and then 3 cc. of petroleum ether. Seven cc. of petroleum

ether are shaken with one drop of  $H_2SO_4$  until the acid is completely broken up into small drops. The mixt. is then quickly poured into the test-tube. The drops of acid sink to the bottom, the violet color forming in the petroleum ether as they sink. E. S.

**Oil from Aleurites species.** C. D. V. GEORGI. *Malayan Agr. J.* 10, 202-5 (1922).—The species *Aleurites moluccana*, candle nut, contains 62% of oil of which 75 to 80% can be expressed. The consts. found were  $d_{40}^{20}$  0.9293,  $n_{20}^{20}$  1.4773, sapon. no. 193.3, I no. 149.0, titer of fatty acids 12.5°, mean mol. wt. of fatty acids 282.4. E. S.

**Experiments with a growth-impregnated charcoal catalyst.** ALWYN PICKLES. *Chem. Age* (London) 8, 166 (1923).—Twigs of willow were grown in  $Ni(NO_3)_2$  and  $NiH_4NO_3$  soln. (50 g. per l.). After carbonization and powdering, the charcoal was reduced at red heat with  $NH_3$  gas. Com. linseed oil was hydrogenated at 1 atm. pressure at temps. of 150°, 160°, 170° and 180°. The charcoal powder contd. 30% of Ni and was used at the rate of 1 g. per 100 cc. oil. The I no. was reduced from 183 to 166 in 70 min. at 150°, to 128 in 70 min. at 160°, to 107 in 70 min. at 170° and to 104 in 70 min. at 180°. The efficiency of the charcoal appeared to be well maintained and removal of the charcoal from the oil presented no difficulty if the filtration was carried out while hot. E. S.

**Problems connected with the saponification of fatty oils.** H. M. LANGTON. *J. Soc. Chem. Ind.* 42, 51-7T (1923).—Three-ton charges of tallow, palm oil, palm-kernel oil, linseed oil and whale oils were autoclaved under the following standard conditions: (1) Steam pressure of 120 lbs. (2) The amt. of base used (CaO or MgO) was 2 1/4% of the wt. of oil. (3) Time 10 hrs. A study of the results shows: (1) The curves are of the exponential type, being characterized by a slow initial stage followed by a rapid 2nd stage when about 90% of the oil is saponified in the 1st few hrs., after which the rate of reaction is retarded. (2) In the case of oils with an initial low content of free fatty acids the reaction curve is at first concave to the vertical axis, denoting that at this stage the reaction is being accelerated. (3) Several of the curves exhibit a marked flattening at points in the neighborhood of the 4th to the 6th hr., suggestive of a tendency for equil. to be established between the reactants and the resultants. (4) MgO is the most effective base in the case of tallows, palm-kernel oil, and the whale oils, lime being superior in the case of palm oil, but in the case of linseed oil the rate and extent of hydrolysis are the same for each base. (5) Considering results where MgO was used, tallows were hydrolyzed most quickly and in decreasing order come whale oils, linseed oil, palm oil and palm-kernel oil. Beef tallow is hydrolyzed more rapidly than mutton tallow. In the case of the 2nd point where the reaction is accelerated which is contrary to what would be expected from the law of mass action which requires that from being great at the start the reaction should be continuously retarded: here is proof of Treuh's contention that in an emulsion the seat of the reaction between the fatty oil and  $H_2O$  is in their surface of contact. Regarding the 3rd point, the belief that equil. is established during sapon. has given rise in some works to the practice of blowing the glycerol soln. from the autoclave after 4-5 hrs. L. finds no advantage in this. E. S.

**Kaffir melon oil.** CHAS. F. JURITZ. *S. African J. Ind.* 6, 67-8 (1923).—Analyses of Tsamma and Monketaan seeds obtained in 1920 contg. 12.85 and 22.1% oil, resp. The consts. of the former were:  $d_{40}^{20}$  0.917,  $n_{40}^{20}$  1.4684, I no. 131.5, sapon. no. 161.1, acid no. 1.8, and of the latter:  $d_{40}^{20}$  0.930,  $n_{40}^{20}$  1.4668, I no. 118.8, sapon. no. 187.9, acid no. 5.8. E. S.

**Examination of colored technical wax preparations.** H. SMELKUS. *Chem.-Zig.* 47, 168-9 (1923).—A steam distn. is made to remove volatile solvents and a distn. with xylene on another sample gives the  $H_2O$ . Alc. is detd. by the sp. gr. of the distillate. To detect colors the distn. residue is dissolved in benzine or ether (nigrosine is insol.) and the colors are sepd. with dil. HCl. Soaps are sepd. by dissolving out with  $H_2O$ . By

detg. the acid and sapon. nos. of the sapond. and unsapond. constituents, and comparing with the known const. of standard waxes, the compn. of the mixt. can be detd.

E. SCHERUBEL

Soap. ANON. *Bur. Standards, Circ. No. 62*, 3-24(1923).—This circular contains a brief discussion of the compn. of soap and of the most important varieties of soap with an outline of certain mfg. processes. Detailed specifications, including methods of sampling and testing, are given for laundry soap for use with soft and with hard  $H_2O$ , and for milled toilet soap.

E. SCHERUBEL

Industrial importance of the metallic soaps. H. I. JONES. *Chem. Met. Eng.* **28**, 489-91(1923).—Most metallic soaps are prepd. by pptn. and when dry are as insol. in gasoline, alc., and  $CHCl_3$  as they are in  $H_2O$ . The freshly prepd. wet soap is readily sol. The soln. in paraffin oils works the same as gasoline and the oil emulsions of the metallic soaps take up an enormous amt. of  $H_2O$ . The temp. of the pptn. is an important factor in obtaining the true colloidal state. It has been found that the addn. of colloidal waxes such as lanolin or beeswax has a stabilizing effect on the colloid. Such solns. may be evapd. and the wax heated to  $45^\circ$  for weeks without the colloid being affected. A mixt. of colloids is more stable than a single pure one. Pure metallic palmitates and stearates are almost impossible to maintain as colloids without the addn. of one of these waxes. The properties of the various metallic soaps have caused them to be put to a great no. of uses, such as lubricating greases, paint and varnish driers, waterproofing of cement and fabrics, medicines, and dry cleaning. E. S.

Petroleum oils obtained from castor oil and from shea butter (MAHLE) **22**. The active principles of some South American plants (JURITZ) **11D**. Apparatus for extracting liquids from cotton seed or other materials by pressure and centrifugal action (U. S. 1,449,290) **1**. Oil filter (U. S. 1,450,750) **1**. Petroleum from vegetable oils (Japan. pat. 40,623) **22**.

EIBNER, ALEXANDER: *Ueber Fette, Oele, Leinölersätmittel und Oelfarben*. München: B. Heller. 488 pp.

Purifying vegetable oils. F. M. TURNER. U. S. 1,448,581, Mar. 13. Cottonseed oil, coconut oil, peanut oil, etc., is sepd. from particles of meal, mixed with  $H_2O$ , treated with steam under pressure and the  $H_2O$  is then sepd. from the oil, to effect purification.

Refining oils. F. M. TURNER. U. S. 1,448,582, Mar. 13. Crude cottonseed or coconut oil or other vegetable or animal oil or fat is treated with a neutralizing agent to remove free fatty acids while under vacuum and all the moisture associated with the material is removed so that the soap and oil are rendered anhyd. and the soap is insol. in the oil.

Removing free acids from saponifiable oils. KIYOSHI MATSUI and the HAMANO SHÔJI KABUSHIKI KAISHA. Japan. 40,511, Nov. 4, 1921. Dried porous matter, such as coke, volcanic lava, pumice stone, etc., of diam. 0.2-10 cm. is immersed in a satd. soln. of KOH or NaOH, dried, filled into a long Fe tube, and heated at  $80-100^\circ$ . Dried oil, previously heated at  $80-100^\circ$ , such as castor oil, etc., is sprayed down through the tube, while  $H_2$  or  $N_2$  is gradually passed upward through it.

Cleansing composition. S. P. KILLY. U. S. 1,449,330, Mar. 20. A cleansing compn. which has healing properties and is adapted for use on the hands is formed of sawdust 1 gal. (impregnated with paraffin oil 24 oz.) and a soln. in  $H_2O$  32 oz. of horax 2 oz.,  $Na_2CO_3$  8 oz. and soap chips 6 oz.

Treatment of waste nickel catalyzer. KOJI NAGASATO and the GOMEI KAISHA

SUZUKI SHOTEN. Japan, 40,684, Nov. 17, 1921. Catalyst for hardening oil is re-covered without destroying the mixed oil and catalyst support, such as asbestos. The catalyst is warmed with dil.  $H_2SO_4$  to form  $NiSO_4$ . The mixt. is sep'd. by the difference of density. The  $NiSO_4$  soln. is filtered and recrystd., and the hardened oil and asbestos are suitable for use after washing with water.

## 29—LEATHER AND GLUE

ALLEN ROGERS

The electrophoresis of chromic solutions. F. L. SEYMOUR-JONES. *Ind. Eng. Chem.* 15, 265-6(1923).—Solns. of  $CrCl_3$ ,  $Cr_2(SO_4)_3$ , and Cr alum, violet and green, normal and rendered basic with NaOH, were subjected to electrophoresis. Cathodic migration of Cr invariably occurred, while anodic migration of green Cr-ion occurred only with the basic sulfate. The basic chloride tanned hide powder normally. Tervalent Cr in a negative complex is, therefore, not the active tanning agent, as postulated by Thompson and Atkin (*C. A.* 16, 3010).

F. L. SEYMOUR-JONES

Acidity of tan liquors from the bacteriological point of view. P. HAMPSHIRE. *Bull. Bur. Bio-tech.* 1, 249-51(1923).—Acidity may be caused by the formation of acetic acid by *Acetobacter* from alc. produced by other bacteria or yeasts from sugars and by the oxidation of glucose to gluconic acid by certain species of *Acetobacter*. An important part is also played by bacteria of the lactic acid group, of which in tan liquors very little is known. The suggestion that putrefactive bacteria survive the acidity of the liquors and, by hydrolyzing hide substance, provide for the nitrogen requirement of the acidogenic organisms, is incorrect. The coli-aerogenes group may also be important in producing acid, but little attention has been paid to this group as yet.

F. L. SEYMOUR-JONES

The question of the  $p_H$  for detannization. R. SCHELL. *Cuir* 12, 38; *J. Soc. Leather Trades' Chem.* 7, 71-3(1923).—The  $p_H$  of tan liquors affects tannin fixation by hide powder greatly, the max. being at  $p_H$  2-3. Accepting the Wilson-Kern definition of tannin and the irreversibility of the hide-tannin compd., their method (*C. A.* 15, 3766) offers the advantage of not depending on the acidity nor on the amt. of hide powder used.

F. L. SEYMOUR-JONES

The preparation of leather for analysis. LLOYD BALDERSTON. *J. Am. Leather Chem. Assoc.* 18, 154-60(1923).—Description of a machine for slicing leather, which facilitates the prepn. of uniform samples for analysis, and avoids changes in compn. of the leather caused by local heating where the sample is prepd. by sawing or rasping.

H. B. MERRILL

Chrome leather analysis: methods used by the sub-committee. D. WOODROFFE. *J. Soc. Leather Trades' Chemists* 7, 90-3(1923); cf. *C. A.* 16, 1889; 17, 1166.—Methods of analysis are given for the following constituents: moisture, grease and S, water solubles dried, water solubles ignited, basicity of the insol. Cr salt on the fibers, sol. ash, total alkali as sulfates, Cr sol. in petroleum ether, free S, total ash,  $CrO_3$  (3 methods), Cr on leather extd. with petroleum ether and water,  $SO_4$  in same leather, petroleum ether ext. ignited, and total alkali.

W. H. BOYNTON

Note on the formation of gelatin from hide powder. F. L. SEYMOUR-JONES. *J. Soc. Leather Trades' Chemists* 7, 93-4(1923).—89.7% of hide substance is hydrolyzed in 5 hrs. from a satd. sample contg. 90.76%. Owing to the small sample (1 g.) no great accuracy can be claimed for the results tabulated.

W. H. BOYNTON

Direct determination of plumping power of tan liquors. J. A. WILSON AND A. F. GALLUN, JR. *Ind. Eng. Chem.* 15, 376-7(1923).—The degree to which a skin will be plumped by a given tan liquor, in any stated length of time, can be measured by the

increase in resistance to compression of a standard piece of skin after immersion in the liquor. Great accuracy in the detn. is possible, even under tan yard conditions.

J. A. WILSON

A new instrument for testing glue and gelatin jellies. WM. D. RICHARDSON. *Chem. Met. Eng.* 28, 551-2(1923); 1 illus.—The Bloom gelometer has two factors, diam. of plunger and depth of plunge, maintained const., while the remaining factor, time of application of the pressure applied by means of flow of shot, is kept within a close time limit. Action is automatic and is fully explained. The instrument should be used in conjunction with a thermostat bath capable of regulation to within  $0.1^\circ$  at  $10^\circ$ .

W. H. BOYNTON

The clarification of glue solutions. ANON. *Farben-Ztg.* 28, 951(1923).—Review.

F. A. WERTZ

The hygroscopicity of hide glues and the relation of tensile strength of glue to its moisture content. E. BATEMAN AND G. G. TOWN. *Ind. Eng. Chem.* 15, 371-5(1923).—Using a high-grade "standard" hide glue [apparent grade = Coopers A. Extra +] and a low-grade hide veneer glue [probably = Coopers  $1\frac{1}{2}\pm$ ], the authors find the hygroscopicities nearly the same, indicating the probability that all hide glues would eventually hold the same moisture at equal humidity and temp. When the moisture reaches 30%, the glue is weaker than wood. Since glue will not mold below 33% moisture, humidity would ruin the joint before mold could be effective. [No mention is made of the antiseptics in these particular specimens. Abstr.] The tensile strength of glue may vary from 20,000 lbs. per sq. in. to almost 0, depending on  $H_2O$  content and grade. The specimens tested showed, with 30%  $H_2O$ , tensile strengths of 1700 and 700 lbs. per sq. in., resp.

JEROME ALEXANDER

TEESDALE, CLYDE HARRY: **Modern Glues and Glue Testing.** Grand Rapids, Mich.: Periodical Publishing Co. 192 pp.

Leather. HIDEO KIKUCHI. *Japan.* 40,577, Nov. 9, 1921. Leather tanned as usual with Cr oxide soln. is suspended in a special soln. (A) for 3 weeks. It is then washed with  $H_2O$ , neutralized with 1.5% borax soln., washed with  $H_2O$  and painted with a milky mixt. of 10 parts of castor oil, 8 parts of Marseilles soap and 50 parts of  $H_2O$ . In the first tanning, the soln. should contain 0.2% Cr oxide and 3% NaCl, the basicity of which is 0.7. In the finishing the soln. should contain 1.1% Cr oxide and 2% NaCl, basicity 0.95. (A) is prepd. as follows: A soln. of  $Na_2SiO_3$  100 in  $H_2O$  500 is gradually added to a mixt. of concd. HCl 86.5 and  $H_2O$  750 parts with agitation and dild. to 1,660 with  $H_2O$ , and then further dild. with  $H_2O$  and HCl until it contains 0.7% silicic acid and acidity 0.05 N. During the process, the concn. of silicic acid and acidity are increased until it contains 2% acid and acidity 0.1 N. The product is very resistant to friction.

Imitation leather. MATABEI YOSHIOKA. *Japan.* 40,463, Oct. 28, 1921. A mixt. of perilla oil 20, tung oil 10 and Pb oxide 0.3 is boiled for a few hrs., cooled, mixed with AcOH 7.5 and painted on a cloth formerly coated with a rubber soln. Then it is coated with an acetone or ether-alc. soln. of celluloid or nitrocellulose. The product is flexible and lustrous.

Tanning composition from acid oil sludge. W. MOELLER. U. S. 1,448,278, Mar. 13. The acid residue of mineral oil refining is treated with an amt. of hydrocarbon, e. g.,  $C_{10}H_{18}$  or  $C_{14}H_{10}$ , corresponding to the excess  $H_2SO_4$  present and the mixt. is heated to complete  $H_2O$  soly. in the presence of  $CH_2O$  and subsequently treated with an excess of alkali to obtain a tanning compn. which may be used with mangrove ext. to increase its soly. under heat and pressure.

Apparatus for drying gelatin. SEIDO MIYOSHI. Japan. 40,619, Nov. 14, 1921.

### 30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

**Lampblack in rubber mixings.** E. MARCEWALD AND F. FRANK. *Gummi-Ztg.* 36, 1459-62(1921); 37, 5-8(1922); *J. Soc. Chem. Ind.* 41, 906A.—A comparison of several grades of German lampblack with an American gasblack showed that vulcanized rubber contg. the gasblack had a higher tensile strength and elongation but had less resiliency than the rubber contg. any grade of lampblack. In compds. of the type: rubber 55, S 5, PbO 5, ZnO 10, lamp or gasblack 25, gasblack gave a greater resistance to tearing, but a lower resistance to destruction by repeated applications of a given load than did lampblack. Microscopical examn. gave no satisfactory explanation of the difference in properties imparted to vulcanized rubber by lampblack and by gasblack.

C. C. DAVIS

**The cold vulcanization of rubber.** E. KINDSCHER. *Mon. sci.* 13, 15-9(1923).—A review.

C. C. DAVIS

**Some experiments on tearability.** B. B. EVANS. *India Rubber J.* 64, 815-9 (1922).—Quant. data are given of the stresses necessary to tear cured rubber compds. Sep. mixts. of rubber and excess S were made, contg. ZnO, refined china clay and light MgCO<sub>3</sub> in equal proportions (1) by wt. and (2) by vol. Series (2) was also repeated with an ultra-accelerator. From each mixing 2 sep. strips were plied together and united by vulcanization. Graphs show the loads to sep. the joined surfaces. The compds. contg. ZnO showed the greatest resistance to tearing and those contg. clay the least. The accelerator increased the resistance to tearing, except when used with a deficiency of S. Overcure decreased the resistance to tear. The direction of the grain in the test pieces had no appreciable influence on the results.

C. C. DAVIS

**A theory on calender grain.** R. W. LUNN. *India Rubber J.* 62, 831-2(1921).—A theory is developed for explaining calender grain on the assumption that rubber is composed of spheres of a viscous liquid enveloped by an elastic skin of low extensibility. These spheres tend to return to their original form since they are incompressible and deformation places them under stress by increasing their area. On release of calender pressure there occurs in the spheres (1) a shortening of the elongated axis, causing the "crawl" of hot sheets; (2) a lengthening of the shortened axis, increasing the thickness of the sheet and (3) a lengthening of the axis vertical to axes (1) and (2), producing greater symmetry and increasing the width of the sheet during "crawl." Chilling makes the liquid in the spheres so viscous that recovery is retarded. During elongation of cured rubber, the spheres are changed to ellipsoids, so that a test piece cut along the grain has less elongation and greater tensile strength than one across the grain. This greater strength and lower elongation are due to the fact that the particles in the piece along the grain are already ellipsoids and have previously suffered part of their total elongation, and to the fact that there are more particles per unit width to resist stress and thus increase the tensile strength.

C. C. DAVIS

**Persistence of calender grain after vulcanization.** W. B. WEIGAND AND H. A. BRAENDLE. *Ind. Eng. Chem.* 15, 259-62(1923).—A quant. detn. of the "grain effect" in cured rubber compds. This effect is expressed as the % difference in "across grain" and "with grain" values of the resilient energy, the latter in turn being expressed as the (1) integrated rotation of the stress-strain curve, (2) integrated energy at rupture and (3) lateral shifting of the stress-strain curve or displacement of the rubber phase. Grain is a function both of the rubber phase and of the pigment phase and its magnitude is dependent to a large extent upon the type of compd. and to a less extent upon



the conditions of cure. The effect due to the rubber phase can be preserved or destroyed by preventing or by allowing distortion during cure, whereas that due to the pigment phase can be modified but not destroyed. The grain persists after curing both in pure gum and in heavily compounded stocks (cf. C. A. 15, 3915; 16, 855; and preceding abstract). It increases not only with the vol. of pigment but greatly so in the presence of acicular crystals, such as  $\text{CaSO}_4$ . C. C. DAVIS

Effect of pigments on temperature of tire treads. D. F. CRANOR. *India Rubber World* 68, 429-31(1923).—Data are given of the rise in temp. while running of tire treads contg. carbon black,  $\text{ZnO}$ , clay and glue. In each case the compds. contd. 20 vols. of pigment per 100 vols. of rubber, with quinoidine as accelerator. The  $\text{ZnO}$  tread under ordinary service remained 15-25° cooler than that contg. carbon black, but less difference was found with hot roads, high speeds and under-inflation. In most tests the clay tread became slightly warmer than the  $\text{ZnO}$  tread. The rise in temp. of the glue tread was intermediate between the carbon black and the  $\text{ZnO}$  treads. Temp. rise was a function of the inflation, load, speed, temp. of the air, temp., dryness and color of the road, length of run, construction of the tire and the compn. of the rubber compds. C. C. DAVIS

The colloid mill. ANON. *India Rubber World* 68, 425-6(1923).—An illustrated description of the Plauson mill (cf. C. A. 16, 174, 450, 664, 1519). Data give the particle size of rubber pigments before and after milling. C. C. DAVIS

The preservation and packing of latex for shipment. B. J. EATON. *Malayan Agr. J.* 10, 151-4(1922).— $\text{NH}_3$  in the proportion of 2% 0.88 soln. on the vol. of the latex is recommended for the preservation of latex. It would probably be more economical to import  $\text{NH}_4$  sulfate or chloride rather than  $\text{NH}_3$  soln.  $\text{NH}_3$  gas from cylinders can be used. G. S. WHITBY

Latex and rubber from young trees. O. DE VRIES. *Comm. Central Rubber Stat. Buitenzorg* 1922, No. 31, 296-309.—In the rubber from trees between 6 and 15 years old the differences in properties are small. With trees 3 to 4½ years old, however, the rubber content of the latex was low and the sp. gr. tended to be high. The rubber, especially in the form of sheet, showed marked "shortness," and the viscosity was very low, particularly for crepe. The rate of vulcanization proved exceptionally high, while in "slope" and tensile strength the vulcanized rubber was inferior to the product from older trees. J. S. C. I.

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Latex-casein top sizing process (KAYE) 23.

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Reclaiming rubber associated with fiber. R. A. TERRHUNE. U. S. 1,450,462, Apr. 3. Rubber waste is treated with an acid, e. g., 30° Bé.  $\text{H}_2\text{SO}_4$ , at 60-100° for a short time, usually about 24 hrs., to destroy the strength of the fiber and prep. the rubber for sepn. and reuse.

Rubber vulcanization. S. M. CAWELL. U. S. 1,449,493, Mar. 27. Dipiperidylthiuramsulfide is used as a vulcanization accelerator. Cf. C. A. 17, 1560.







